

Accounting for Aerosol Scattering in the Remote Sensing of Greenhouse Gas

Thesis by
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Doctor of Philosophy

The Caltech logo, featuring the word "Caltech" in a bold, orange, sans-serif font, centered within a light orange rectangular background.

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To my family.

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ABSTRACT

This thesis includes three different projects related to the remote sensing of Earth's atmosphere. The first part, comprising Chapter 2 and Chapter 3, focuses on the retrieval of Level 1 product, particularly the effect of aerosol scattering in the remote sensing of greenhouse gases. In Chapter 2, we study the aerosol induced bias in the retrieval of column averaged CO₂ mixing ratios (X_{CO_2}). Ground based remote sensing data from the California Laboratory for Atmospheric Remote Sensing Fourier Transform Spectrometer (CLARS-FTS) are used. We employ a numerical radiative transfer model to simulate the impacts of neglecting aerosol scattering on the CO₂ and O₂ slant column densities (SCDs) operationally retrieved from CLARS-FTS measurements. These simulations show that the CLARS-FTS operational retrieval algorithm likely underestimates CO₂ and O₂ abundances over the LA basin in scenes with moderate aerosol loading. The bias in the CO₂ and O₂ abundances due to neglecting aerosol scattering cannot be canceled by ratioing each other in the derivation of the operational product of X_{CO_2} . We propose a method for approximately correcting the aerosol-induced bias. Results for CLARS X_{CO_2} are compared to the direct-sun X_{CO_2} retrievals from a nearby Total Carbon Column Observing Network (TCCON) station.

In Chapter 3, we explain why large X_{CO_2} retrieval errors are found over deserts in the space borne Orbiting Carbon Observatory-2 (OCO-2) data. We argue that these errors are caused by the surface albedo being close to a critical surface albedo (α_c). Over a surface with albedo close to α_c , increasing the aerosol optical depth (AOD) does not change the continuum radiance. The spectral signature caused by changing the AOD is identical to that caused by changing the absorbing gas column. The degeneracy in the retrievals of AOD and X_{CO_2}

results in a loss of degrees of freedom (DOF) and information content (H). We employ a radiative transfer model to study the physical mechanism of X_{CO_2} retrieval error over a surface with albedo close to α_c . Based on retrieval tests over surfaces with different albedos, we conclude that over a surface with albedo close to α_c , the X_{CO_2} retrieval suffers from a significant loss of accuracy.

The second part, mainly in Chapter 4, focuses on the application of Level 2 product. In this Chapter, we examine the uncertainties in middle atmospheric HO_x chemistry by comparing the Aura Microwave Limb Sound (MLS) OH and HO_2 measurements with the simulations of the Caltech-JPL KINETICS photochemical model. The model using the standard chemical kinetics underestimates OH and HO_2 concentrations in the mesosphere. To resolve the discrepancies, we use MLS OH and HO_2 measurements as benchmark to adjust the involved chemical rate coefficients within reasonable uncertainty ranges with an optimal estimation algorithm. The results show that four key reaction rate constants and the O_2 cross section at Lyman- α (121.6 nm) are the most sensitive parameters for determining the HO_x profiles. We conclude that the rate coefficient of $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ requires a very large adjustment beyond the uncertainty limits recommended in the NASA Data Evaluation, which suggests the need for future laboratory measurements. An alternative explanation is that radiative association plays a significant role in this process, i.e. $\text{H} + \text{O}_2 \rightarrow \text{HO}_2 + h\nu$, which has never been measured or computed.

In the Appendix, we put in a Chapter based on my work with Prof. Andrew Thompson on ocean submesoscale turbulence.

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2. **Zhang, Q.**, A. F. Thompson, and A. Lazar (2016), Submesoscale Turbulence over a Topographic Slope. *Ocean Modelling*, submitted. Q.Z. did the modelling, analyzed the model output, and wrote a large part of the manuscript.
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Chapter 1

INTRODUCTION

Increased understanding of the impacts of greenhouse gases (GHGs) on climate change depends critically on the measurement of their concentrations [IPCC AR5, 2013]. Urban areas, such as the megacity of Los Angeles (LA), California, are immense sources of global GHGs. These areas, which contain more than 50% of the world's population, are contributing at least 70% of fossil fuel CO₂ emissions and a large amount of anthropogenic CH₄ [Duren and Miller, 2012; Kort *et al.*, 2012]. In the past decade, satellite observations such as those from the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), the Greenhouse Gases Observing Satellite (GOSAT), and the Orbiting Carbon Observatory-2 (OCO-2) have been proposed to measure the global distribution of CO₂ [Bovensmann *et al.*, 1999; Crisp *et al.*, 2004; Kuang *et al.*, 2002; Yokota *et al.*, 2009]. Since CO₂ is well mixed in the atmosphere, retrieval precision up to ~1 ppm is typically required for CO₂ flux inversion [Miller *et al.*, 2007]. Such data could significantly reduce the uncertainties in the regional CO₂ flux estimation [Rayner and Brien, 2001].

According to the IPCC AR5 report, there is very high confidence that current GHG concentrations have exceeded the ice core record in the past 22,000 years. The increase is mostly attributed to the anthropogenic emissions in the industrial era. Figure 1.1 shows the changes of major GHGs over the past two centuries and the

anthropogenic contribution to the total CO_2 emission. To eliminate the uncertainties in the estimation of GHG emission and future climate projections, we must make global accurate measurements and continuously monitor the GHG concentration. For this purpose, remote sensing is an ideal approach due to its high sampling frequency and wide coverage.

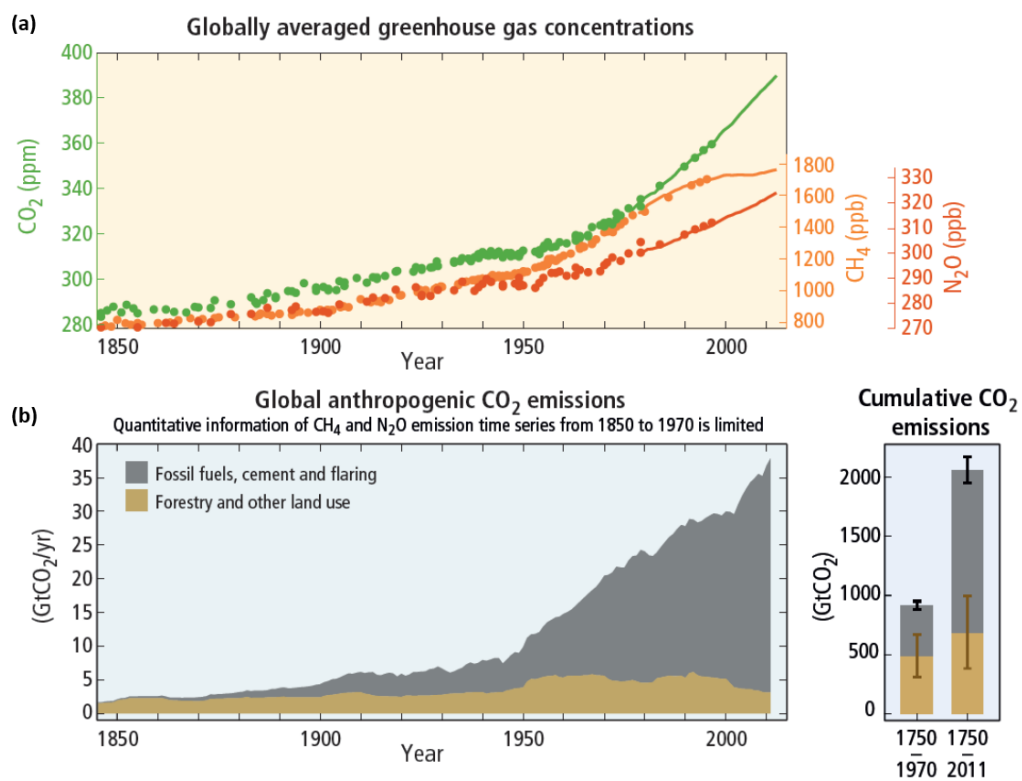


Figure 1.1. (a) Atmospheric concentrations of the greenhouse gases carbon dioxide (CO_2 , green), methane (CH_4 , orange) and nitrous oxide (N_2O , red) determined from ice core data (dots) and from direct atmospheric measurements (lines). (d) Global anthropogenic CO_2 emissions from forestry and other land use as well as from burning of fossil fuel, cement production and flaring. [IPCC, 2004]

Figure 1.2 illustrates the retrieval algorithm currently used by the OCO-2 mission. The retrieval process starts with Level 1B product, which is the calibrated spectral radiance measured from space. The “pre-screening” process removes data of poor quality or contaminated with large aerosol/cloud optical depth. Then, other external data, such as pointing geometry, atmospheric profile and gas absorption coefficients are used by the radiative transfer model to compute the simulated spectral radiance. In the inverse model, the statevector is updated until the simulated radiance matches the measurement and the retrieval converges. The optimal estimation of the statevector is achieved by minimizing the cost function as in Equation 1.1.

$$\chi^2 = [x_i - x_a]^T \mathbf{S}_a^{-1} [x_i - x_a] + [y - \mathbf{F}(x_i)]^T \mathbf{S}_e^{-1} [y - \mathbf{F}(x_i)] \quad (1.1)$$

where x_a is the statevector, $\mathbf{F}(x)$ is the forward model, y is the measurement, \mathbf{S}_a is the *a priori* covariance matrix, and \mathbf{S}_e is the measurement error covariance matrix [Rodgers, 2000].

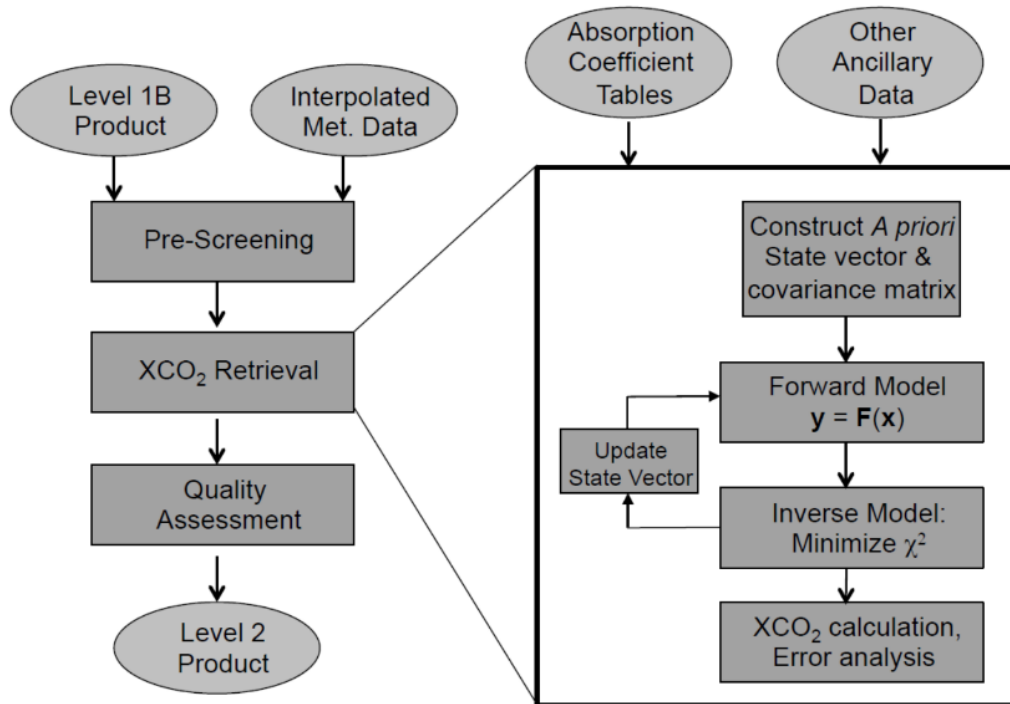


Figure 1.2. OCO-2 retrieval algorithm [O'Dell *et al.*, 2012]. Level 2 product is retrieved from the Level 1B spectra by minimizing the cost function. The forward model in the retrieval algorithm relies on many external parameters such as the absorption coefficient table, observation geometry, and aerosol optical properties.

Aerosol scattering is often considered the major source of error in the remote sensing of GHGs [Aben *et al.*, 2007]. Scattering in the atmosphere could change the photon path distribution, thus altering the apparent absorption of the target trace gas [Oshchepkov *et al.*, 2008]. Operational trace gas retrieval algorithms for space missions often apply simplified aerosol models due to the lack of information to constrain a large number of aerosol parameters [Frankenberg *et al.*, 2012; Guerlet *et al.*, 2013]. To mitigate the impacts of imperfect aerosol/cloud modeling, these retrieval algorithms perform target scene screening that filters out those observations

contaminated by large aerosol and cloud optical depths (AOD/COD). For OCO-2 mission, $\text{AOD} = 0.3$ is a typical threshold [O'Dell *et al.*, 2012]. The filtering is often imperfect as it depends on many parameters such as viewing and solar geometries, AOD, aerosol type, and aerosol height [O'Dell *et al.*, 2012; Oshchepkov *et al.*, 2012]. Over megacities where aerosols often reside in the urban planetary boundary layer (PBL), a large portion of remote sensing measurements from space are usually filtered out by pre- or post-screening [Crisp *et al.*, 2012; Yoshida *et al.*, 2011]. Hence, there exists a need to fill this “gap” in the satellite measurement databases, e.g., the source areas that significantly contribute to the global GHG emissions. Deserts are also associated with large aerosol loading. Previous studies [e.g., Houweing *et al.*, 2005] have suggested potential problems in the retrieval of GHG over such regions.

This thesis studies the effect of aerosol scattering in the remote sensing of GHG using both ground based and space borne measurements. Both ground-based and space-borne measurements are used. Their goal is to understand how aerosol scattering impacts the measurements of trace gas column abundances and mixing ratios, how to correct for the error caused by aerosols, and how aerosol scattering effect interacts with surface properties.

The remote sensing data processing is often divided into two levels. While the next two Chapters focus on the retrieval of Level 1 product, Chapter 4 is a separate section which focuses on the application of Level 2 retrieval product in calibrating a photochemical model. In this Chapter, we compare the Microwave Limb Sounder (MLS) measurements of odd hydrogen (HO_x) species, including hydroxyl radical (OH) and hydroperoxyl (HO_2) with the simulations of the Caltech-JPL KINETICS

photochemical model. HO_x species are of great interests to the climate community because they are important catalysts for the dissociation of O_3 in the middle atmosphere. Our study indicates that accurate measurements of photochemical rate coefficients and molecular cross sections are crucial in simulating stratospheric and mesospheric HO_x chemistry. High quality satellite observations can be used to constrain or retrieve photochemical parameters and help improve our understanding of atmospheric chemistry.

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Chapter 2

ACCOUNTING FOR AEROSOL SCATTERING IN THE CLARS RETRIEVAL OF COLUMN AVERAGED CO₂ MIXING RATIOS.

2.1. Introduction

To measure GHG concentrations in LA, CLARS-FTS was deployed on the top of Mt. Wilson, looking down at the land surface of target sites in the LA basin [see *Fu et al.*, 2014; *Wong et al.*, 2014 and references therein]. The current CLARS-FTS operational retrieval algorithm (version 1.0) uses measurements of the CO₂ absorption band centered at 1.61 μm to estimate the CO₂ slant column density (SCD) along the line of sight. SCD is defined as the total number of absorbing gas molecules along the optical path per unit area. A modified version of the GFIT program is used in the retrieval [*Fu et al.*, 2014]. The GFIT program was originally used for observing direct sunlight [*Toon et al.*, 1992; *Wunch et al.*, 2011]. Surface reflection is included in the modified version but aerosol scattering is not taken into account. The effect of scattering, on the other hand, is estimated by simultaneously retrieving the O₂ SCD based on measurements of the O₂ absorption band centered at 1.27 μm , assuming that the changes in light path due to aerosol scattering are identical in both the 1.61 μm and 1.27 μm bands. The bias due to aerosol scattering could be mitigated by estimating the column-averaged dry air mole fraction of CO₂ (X_{CO_2}) defined as follows:

$$X_{CO_2} = 0.2095 \frac{SCD_{CO_2}}{SCD_{O_2}} \quad (2.1)$$

This algorithm was designed for retrieving X_{CO_2} in clear sky conditions. However, in the presence of haze, it leads to an underestimation of CO_2 and O_2 SCDs due to the change in photon path length through the boundary layer [Oshchepkov *et al.*, 2012], which is not accounted for in the retrieval. The wavelength and species dependence of aerosol scattering also implies that division by O_2 SCD does not completely remove the aerosol scattering effect in the $1.61 \mu m$ CO_2 absorption band. Therefore, the assumption that aerosol scattering is identical in the two bands leads to an observable bias in the retrieved X_{CO_2} . The CLARS operational algorithm ignores aerosols and instead uses a filter criterion in which data are filtered out if the retrieved and geometric O_2 SCD values differ by more than 10% [Wong *et al.*, 2015]. However, this criterion is somewhat arbitrary. In a megacity where aerosol loading is often non-negligible, it is necessary to evaluate the influence of aerosol scattering on the retrievals of CLARS-FTS measurements.

The aim of this paper is to present the CLARS observations and show the effects of aerosols scattering on the observed radiance and the retrieved absorbing gas abundances. The bias can be understood and mitigated with the help of a full-physics radiative transfer (RT) model. In Section 2.2, we first introduce the CLARS measurements and demonstrate the retrieval bias in the SCDs of CO_2 and O_2 due to neglecting aerosol scattering. In Section 2.3, we show the high resolution spectral signatures of aerosol scattering on the observed radiance using CLARS measurements and a numerical RT model. In Section 2.4, simulations are

performed using CLARS viewing geometries to illustrate how aerosol scattering causes an apparent reduction in the retrieved abundances of trace gases and how wavelength dependence of the scattering causes bias in the X_{CO_2} product. A fast and effective correction approach is presented in Section 2.5, and the results are validated using comparison between CLARS and Total Carbon Column Observing Network (TCCON) measurements in Section 2.6. A discussion of our results and conclusions follows in Section 2.7.

2.2. Underestimation of SCDs due to aerosol scattering

Here we will show the SCD retrieval bias caused by neglecting aerosol scattering. CLARS-FTS has two modes of operation as shown in Figure 2.1 [*Fu et al.*, 2014, supplementary figure 1]: (1) Los Angeles Basin Surveys (LABS) mode using reflected sunlight from the LA basin that undergoes absorption and scattering by trace gases and aerosols below the CLARS site; (2) Spectralon Viewing Observation (SVO) mode using reflected sunlight from a locally positioned Spectralon plate that samples the solar beam above the CLARS site and measures the background GHG abundances in the free troposphere above Mt. Wilson. CLARS-FTS has high sensitivity to the variation of GHGs over the LA basin due to the long light path through the urban planetary boundary layer (PBL) (typically 20 km distance from CLARS site to the LA basin land surface). In the LABS mode, this viewing geometry offers much higher sensitivity to the atmospheric composition within the PBL than a typical satellite geometry but also makes the

measurements more susceptible to the influence of aerosol scattering and absorption.

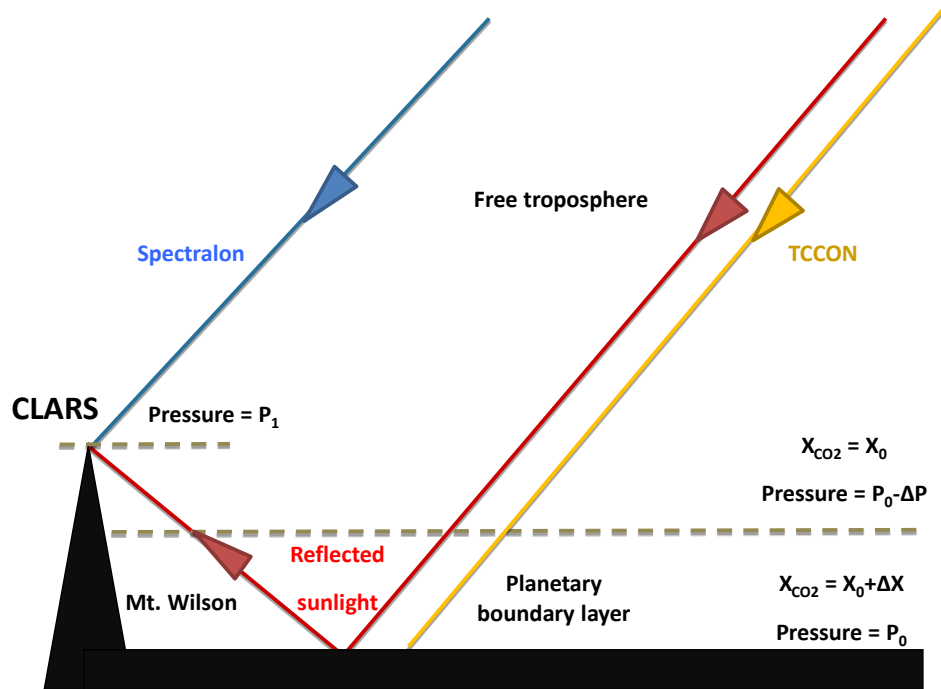


Figure 2.1. Schematic figure of CLARS measurement geometries and validation. The validation method will be presented in Section 2.6. We employ the X_{CO_2} data from the JPL TCCON station (yellow) and CLARS Spectralon (blue) to calculate the mean CO_2 mixing ratio along the West Pasadena reflected light path (red). The background CO_2 mixing ratio is X_0 , and the CO_2 mixing ratio within the PBL is $X_0 + \Delta X$. We assume that the surface pressure is P_0 , the pressure at the top of PBL is $P_0 - \Delta P$, and the pressure at the CLARS instrument is P_1 . P_0 and P_1 are known with high accuracy from the NCEP atmospheric profile.

In the LABS mode, CLARS-FTS points at a programmed sequence of ground target locations in the LA basin. Sample CO_2 SCDs to a target in West Pasadena are shown in Figure 2.2(a). For scenarios over the LA basin with moderate aerosol

loading (aerosol optical depth AOD ~ 0.1 in the $1.61 \mu\text{m}$ band), we obtain a ‘U-shape’ as the SCD of absorbing gas along the line of sight changes from the morning to the afternoon. The data are closer to the 1:1 line in the morning (A-B) and deviate from it as the haze builds up in the afternoon (B-C). For a pure trace gas absorption scenario, i.e. with no aerosol scattering in the atmosphere, we expect the measured SCD to agree with the calculated geometric SCD.

Therefore the data points, such as those in the SVO mode measurements (green "+" points in Figure 2.2), should fall on the 1:1 line. Some systematic errors in the spectroscopic parameters may exist, but their impact on the retrieval is small. For the measurements over West Pasadena, the observed CO_2 SCDs are smaller (by up to 13%) than the geometric ones from the morning to the afternoon. Figure 2.2(b) shows similar deviation (by up to 17%) in the O_2 SCDs. The deviations in CO_2 could arise from diurnal variations (i.e., changes of CO_2 emission rate over the LA basin, etc). However, there are no emission sources or sinks in the LA basin for O_2 . This suggests that the low bias is mainly due to the increase in AOD during the daytime, as indicated by the images recorded by a visible camera that was co-aligned with the CLARS-FTS. Since aerosol scattering has wavelength dependence, we expect the O_2 and CO_2 SCDs to have different deviations from the 1:1 line. Therefore, dividing the CO_2 SCD by the O_2 SCD cannot completely eliminate the bias in X_{CO_2} .

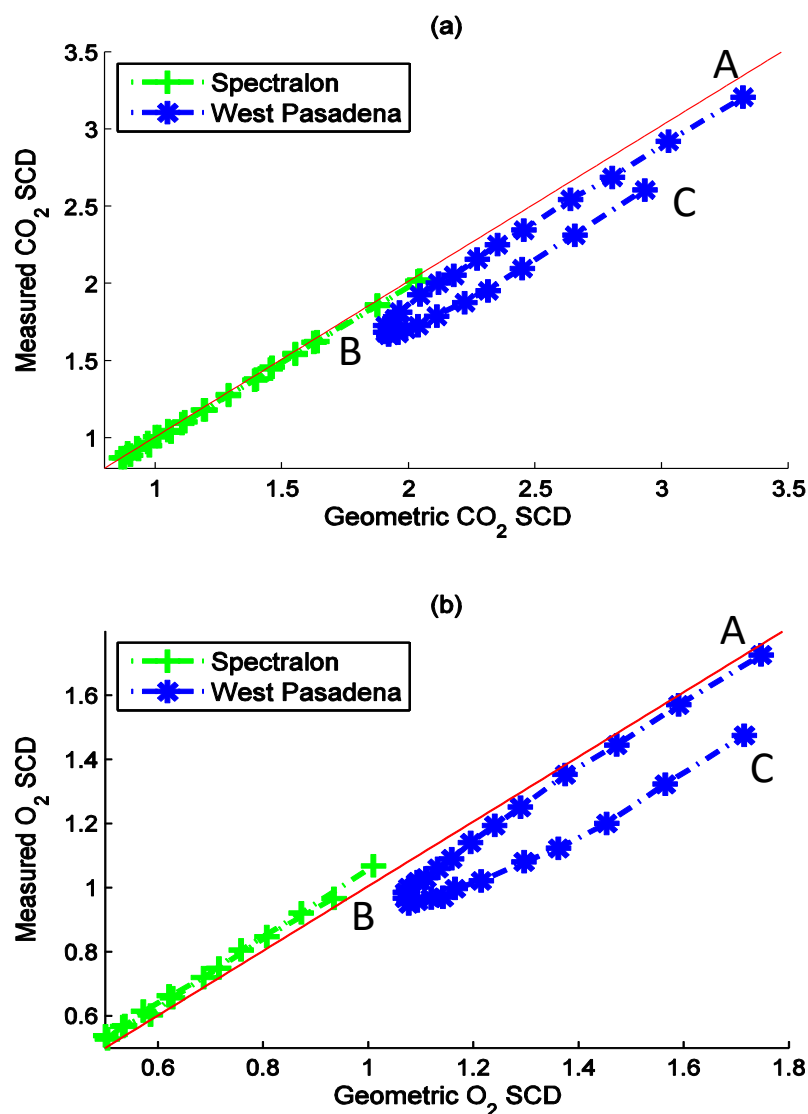


Figure 2.2. Variations of CLARS measured SCD v.s. geometric SCD from the morning to the afternoon, for (a) CO_2 and (b) O_2 . A, B and C indicate morning, noon and afternoon. Units for CO_2 and O_2 SCDs are scaled by 10^{22} and 10^{25} molecule/ cm^2 , respectively. SCD is defined as the total number of molecules along the light path per cm^2 . The units represent abundances of gas molecules in the atmosphere. Geometric SCDs are calculated from the *a priori* atmospheric profiles at Spectralon and West Pasadena. The red lines indicate 1:1 correspondence between measured and geometric SCDs.

2.3. Influence of aerosols on the observed radiance

We simulate the CLARS-FTS spectral radiance using a numerically efficient two-stream-exact single scattering (2S-ESS) RT model [Spurr and Natraj, 2011], where the RT calculation is done analytically except for the boundary value problem (which is also done using a simple and fast pentadiagonal solver rather than typical matrix inversion techniques). The 2S-ESS RT model is also different from a typical two-stream model in that the singly scattered radiation is computed exactly (using all scattering phase function moments), the two-stream approximation is used only for the multiply scattered radiation. The exact single scattering calculation mitigates biases due to the severe phase function truncation inherent to the two-stream approximation. In this model, the *a priori* atmospheric profile has 70 layers from the surface up to 70 km, derived from NCEP-NCAR reanalysis data [Kalnay *et al.*, 1996]. Absorption coefficients for all absorbing gases are obtained from the HITRAN database [Rothman *et al.*, 2008]. We calculate the optical depth for each layer using the Reference Forward Model [Dudhia *et al.*, 2002], and then simulate the reflected radiance observed by the CLARS-FTS. We assume the surface reflection to be Lambertian with a surface albedo of 0.23, as measured for West Pasadena [Fu *et al.*, 2014]. The model takes into consideration Rayleigh scattering by air molecules. The viewing zenith angle, a constant parameter, is 83.1° for the target scene over West Pasadena. The solar zenith angle (SZA) and relative azimuth angle (AZA) at a given time can be calculated as a function of latitude, time and solar declination angle. In the forward model, we convolve the simulated radiance using the CLARS-FTS instrument line shape (ILS)

with full width at half maximum (FWHM) = 0.022 cm^{-1} [Fu *et al.*, 2014]. The spectral resolution is adjustable and the current operational value is 0.06 cm^{-1} . The corresponding instrument maximum optical path difference is 5.0 cm. The signal to noise ratio (SNR) is 300. Gaussian white noise is added to the simulated spectra.

Figure 2.3 (a) and (b) shows synthetic spectra in the $1.6\mu\text{m}$ CO_2 absorption band with different CO_2 abundances and AODs in the PBL. The spectra from the 2S-ESS RT model have been validated against a full-physics RT model VLIDORT [Spurr, 2006], which provides radiances with accuracy higher than the 2S-ESS RT model. In the presence of aerosol, the absorption lines move upward in the core and wing regions. The FWHM of the spectral lines in Figure 2.3(b) shows that the apparent absorption becomes weaker as AOD increases. Intuitively, this is because aerosol scattering shortens the photon path length and reduces absorption within the PBL. The effect is similar to decreasing CO_2 abundance in the atmosphere (Figure 2.3a), as the spectral differences in Figures 2.3 (a) and (b) have almost the same shapes. In the high-resolution CLARS-FTS spectra, this feature can be resolved for individual absorption lines. In Figure 2.3(c), two measurements from CLARS-FTS on 23 March 2013 are shown. The measurements are made in the morning (clear) and in the afternoon (hazy) with nearly identical SZAs. The AOD is estimated based on images from a co-boresighted visible camera. The spectral lines measured in the hazy scenario (red line in Figure 2.3c) move inward and show weaker absorptions, compared with the ones measured in the clear scenario (blue line in Figure 2.3c). This change in photon path length is observed in both the CLARS-FTS measured spectra

(Figure 2.3c) and the simulations (Figure 2.3b). Similarly, the same features are also apparent in the spectra of the O₂ absorption bands.

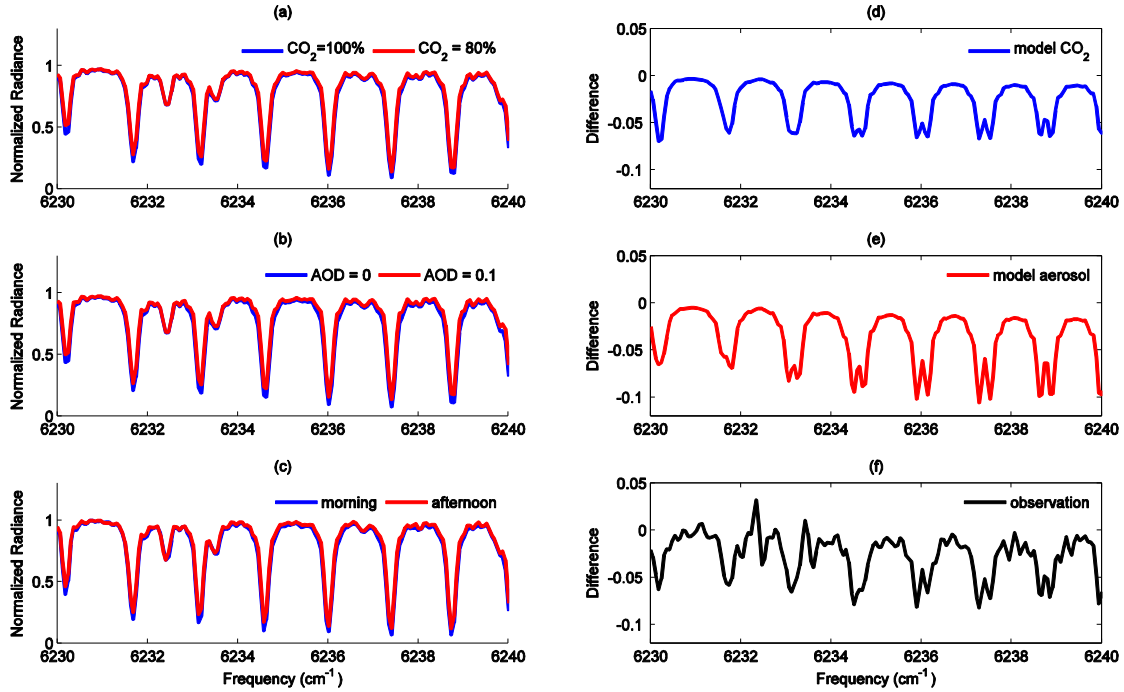


Figure 2.3. Spectra of the CO₂ absorption band. (a) Normalized radiance from the numerical model with different CO₂ abundances. CO₂ abundance is adjusted by multiplying a constant scale factor (80%) to the atmospheric profile. (b) Normalized radiance from the numerical model with different AODs in the PBL. (c) Measurements of normalized radiance from CLARS instrument on 23 March 2013. Measurements in the morning and in the afternoon have similar SZAs (65.16° vs. 64.46°) but different AODs. The right panels (d) ~ (f) are corresponding differences between the spectra in the left panels. Differences in panel (d) and (e) are proportional to the Jacobians of CO₂ scaling factor and AOD.

These features indicate that local aerosol scattering leads to a reduction in apparent absorption. Using normalized spectra, the equivalent effects in the apparent absorption, either caused by reducing absorbing gas abundance or by aerosol

scattering in the PBL, are difficult to distinguish. In a model without aerosol scattering, all the changes in line width are attributed to changes in gas abundance. We assume that the daily gas abundance variations in the LA region are much smaller than that observed in Figure 2.2 (especially for O_2). The model explains the changes in retrieved SCDs from CLARS-FTS as the AOD increases from the morning to the afternoon (Figure 2.2). The effect of aerosol scattering also increases as the SZA becomes larger in the afternoon.

To explain the differences in spectra, we also developed a one-line absorption model for CO_2 and O_2 (Appendix 2.1). Taking CO_2 as an example, Figure 2.A1 shows the calculated reflectance. In this case, the apparent absorption becomes weaker after normalization (by the maximum value of the radiance) as shown in Figure A.1 (b) for $\omega_0 = 0.99$. This suggests that the gaseous absorption is reduced by aerosol scattering. The magnitude of this effect depends on the SSA and aerosol phase function. We also calculate the reflectance with $\omega_0 = 0.2$ as shown in Figures 2.A1 (a) and 2.A1 (c). The reflectance decreases with AOD, but after normalization, we can still see the line-filling. In Figure 4(d), we obtain similar line-filling effects by reducing the concentration of CO_2 in the calculation and setting AOD in the PBL to zero. For an O_2 absorption line centered at $\nu_0 = 7863.4 \text{ cm}^{-1}$, all the features are similar in general (not shown here).

2.4. Measurement bias caused by aerosol scattering

In order to quantify the influence of aerosol scattering on the GHG retrievals and simulate the bias observed by CLARS-FTS, we assume nonzero AOD evenly

distributed in the PBL and use the 2S-ESS model to generate synthetic spectral radiance data. In a forward model with the same configuration, AOD is set to zero and held constant. The forward model is used to fit the synthetic spectra. This approach approximately simulates the influence of neglecting aerosol scattering on the retrieved SCDs. We also neglect the effect of water vapor. The fitting process employs the Levenberg-Marquardt (LM) algorithm [Rodgers, 2000]. The iteration in this algorithm is:

$$\mathbf{x}_{i+1} = \mathbf{x}_i + [(1 + \gamma)\mathbf{S}_a^{-1} + \mathbf{K}_i^T \mathbf{S}_e^{-1} \mathbf{K}_i]^{-1} \{ \mathbf{K}_i^T \mathbf{S}_e^{-1} [\mathbf{y} - \mathbf{F}(\mathbf{x}_i)] - \mathbf{S}_a^{-1} [\mathbf{x}_i - \mathbf{x}_a] \} \quad (2.2)$$

where \mathbf{x}_a is the *a priori* state vector, \mathbf{y} is the measured spectral radiance, \mathbf{S}_a is the *a priori* covariance matrix, \mathbf{S}_e is the spectral radiance noise covariance matrix, \mathbf{K} is the Jacobian matrix, $\mathbf{F}(\mathbf{x})$ is the forward model and γ is the parameter determining the size of each iteration step. The synthetic measurements cover 25 cm⁻¹ wide spectral regions in both the 1.27 μm (O₂) and 1.61 μm (CO₂) absorption bands. The state vector elements to be adjusted are the scaling factors for O₂ and CO₂ abundances. In this study, we set \mathbf{S}_a to be 10% for both O₂ and CO₂ SCD simulations. The results are not sensitive to the value of the *a priori* constraints.

To simulate the observed 'U-shape' as shown in Figure 2.2, AOD data are taken from measurements of the AErosol RObotic NETwork (AERONET) station at Caltech on 23 March 2013 [Holben *et al.*, 1998; Holben *et al.*, 2001]. AERONET measurements cover the wavelength range from 340 to 1020 nm. However, neither the CO₂ nor the O₂ near-infrared band used in our study is included in the AERONET measurements. To calculate the AOD in these two bands, we use the Angstrom exponent law to extrapolate the data [Seinfeld and Pandis, 2006]

$$\frac{\tau}{\tau_0} = \left(\frac{\lambda}{\lambda_0} \right)^{-\kappa} \quad (2.3)$$

where λ_0 and τ_0 are the reference wavelength and the corresponding AOD, and $\kappa = 0.78$ is the Angstrom exponent. Seven wavelengths from 340nm to 1020nm are used in the regression. The AOD in the CO₂ band starting at 1607 nm is 0.0708, while the AOD in the O₂ band starting at 1264 nm is 0.0854. These values are obtained from AERONET by extrapolation.

Aerosol properties in the LA basin are obtained from simulations using the Weather Research and Forecasting [WRF; *Skamarock et al.*, 2005] model. The Modal Aerosol Dynamics Model/Secondary Organic Aerosol Module (MADE/SORGAM) [*Ackermann et al.*, 1998; *Schell et al.*, 2001] is used to obtain specific values for 5 aerosol types (black carbon, organic carbon, sulfate, coarse and accumulation mode sea salt). The aerosol single scattering properties are computed using the Meierhoff Mie code [*Derooij and Vanderstap*, 1984], with size distribution parameters taken from the Optical Properties of Clouds and Aerosols [OPAC; *Hess et al.*, 1998] database. Table 2.1 shows the typical aerosol composition (as percentages of total optical depth) and optical parameters in this region. In the forward model, we vary the SZA and AZA to simulate different measurements from the morning to the afternoon (7:00 am to 5:00 pm). We assume that the total AOD increases from zero to the value measured by AERONET station at 4:48 pm. The temporal variation of AOD is simulated by an idealized function as shown in Equation (2.4).

$$\tau_s = \frac{AOD}{2} + \frac{AOD}{2} \tanh\left(\frac{H}{30^\circ}\right) \quad (2.4)$$

where H is the hour angle varying linearly from -75° (7:00 am) to 75° (5:00 pm). The AERONET measurement of AOD at 4:48 pm is used to constrain Equation (2.4).

Table 2.1. Climatological aerosol composition and optical properties in the LA region.

	Organic	Seasalt (accum)	Seasalt (coarse)	Soot	Sulfate
percentage	4.9%	31.7%	38.1%	7.9%	17.4%
SSA	0.872	0.998	0.985	0.040	0.999
g	0.55	0.79	0.82	0.15	0.69

[Ackermann *et al.*, 1998; Schell *et al.*, 2001]

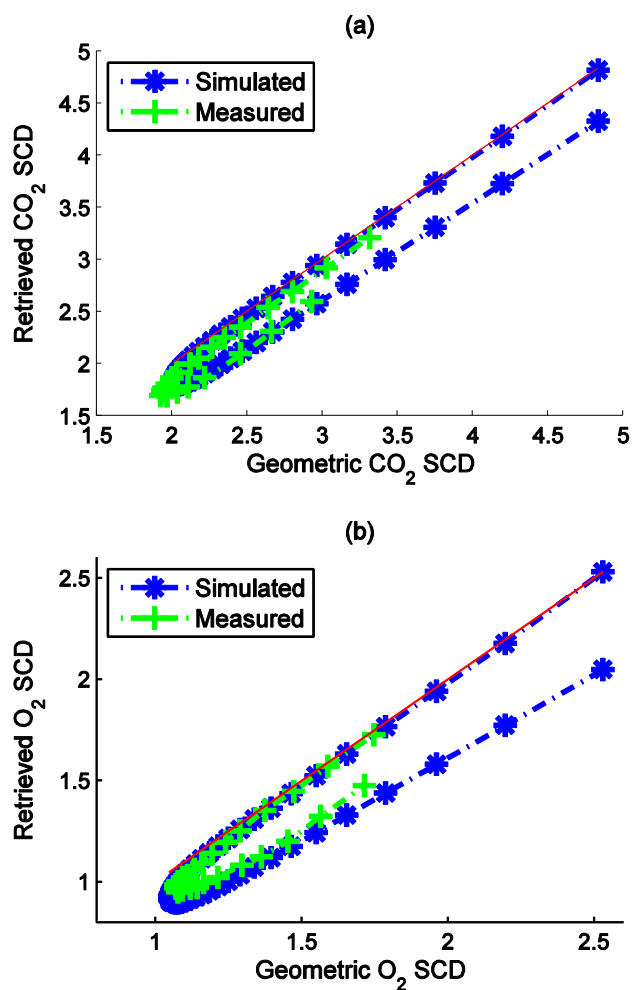


Figure 2.4. Comparison between the simulated and measured SCD daily variations on 23 March 2013 in West Pasadena for (a) CO_2 SCD and (b) O_2 SCD. Units for the CO_2 and O_2 SCDs are scaled as in Figure 2. The red lines indicate 1:1 correspondence between measured and geometric SCDs.

The simulated variations of CO_2 and O_2 SCD are shown in Figure 2.4 and match the CLARS observations. Furthermore, the 'U-shape' of the O_2 SCD also shows a larger low bias than that for the CO_2 SCD for the same aerosol conditions.

This demonstrates that aerosol scattering is the cause of the low bias in the CO₂ and O₂ SCD. SCD biases caused by aerosol scattering are not equal in the two absorption bands and therefore cannot be removed by the ratioing in the calculation of X_{CO2}.

The retrieval bias in the SCDs due to neglecting aerosol scattering can be estimated using the Rodgers method [Rodgers, 2000], as shown in Equation (2.5)

$$\Delta SCD = \mathbf{G}\mathbf{K}_b \cdot \tau_s \quad (2.5)$$

where ΔSCD is the fractional SCD retrieval bias; \mathbf{K}_b is the Jacobian of radiance with respect to AOD τ_s ; $\mathbf{G} = \mathbf{S}_a \mathbf{K}^T (\mathbf{K} \mathbf{S}_a \mathbf{K}^T + \mathbf{S}_e)^{-1}$ is the gain matrix, or the sensitivity of the SCD retrieval to the observed radiance. This method provides a linear estimate of the aerosol influence on the SCD retrieval bias. In the O₂ absorption band, $\mathbf{G}\mathbf{K}_b = -1.94$, $\tau_s = 0.1$ corresponds to a SCD retrieval deficit of 19.4%; in the CO₂ absorption band, $\mathbf{G}\mathbf{K}_b = -1.81$, $\tau_s = 0.1$ corresponds to a SCD retrieval deficit of 18.1%. The bias analysis shows that a typical AOD of 0.07~0.08 causes biases in the CO₂ and O₂ SCD retrieval of up to 13~17%, consistent with the U-shape shown in Figure 2.2. The SCD bias for O₂ is larger than that for CO₂ at the same AOD. As a result, X_{CO2} calculated according to Equation (2.1) would exhibit a high bias.

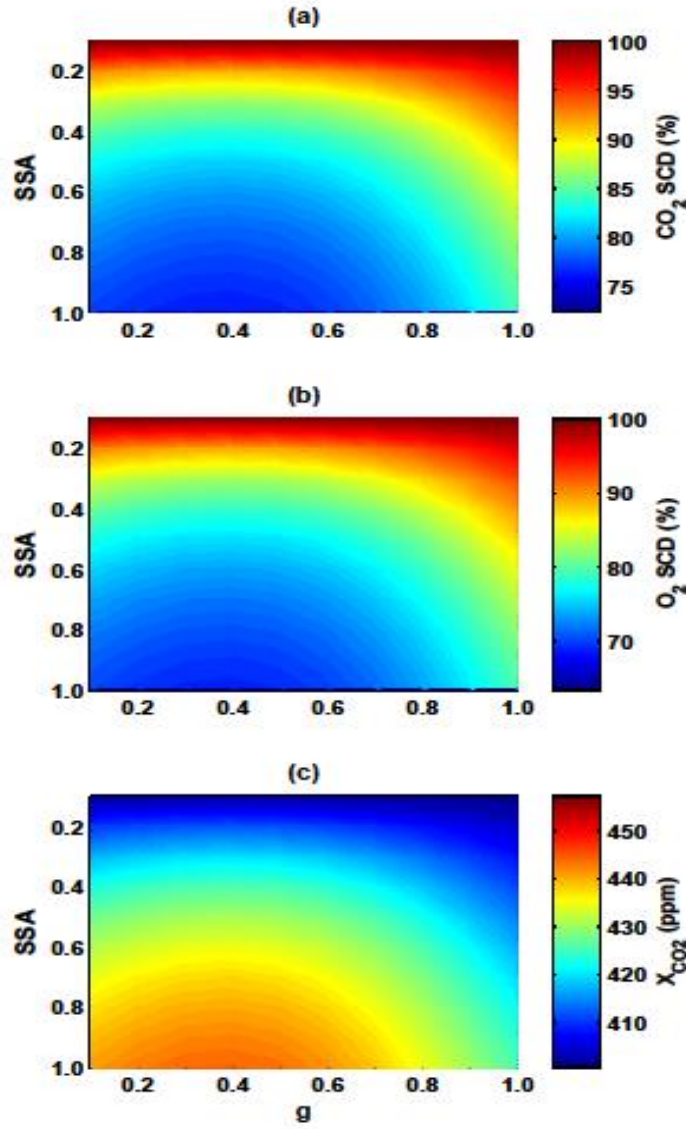


Figure 5. Simulation results when aerosol scattering is neglected for (a) CO_2 SCD (b) O_2 SCD and (c) X_{CO_2} . Effects of different kinds of aerosols are investigated in the SSA-g parameter space with $\text{AOD} = 0.1$ (in the CO_2 absorption band). SCD simulation results are displayed in percentage, 100% corresponds to the true value. The true value of X_{CO_2} is 400.8 ppm. Biases are measured as the deviation from the true value. We use a fixed viewing geometry in the simulations, with $\text{SZA} = 45.2^\circ$, $\text{VZA} = 83.1^\circ$, and $\text{AZA} = 9.7^\circ$.

It is also of interest to study the measurement bias caused by different kinds of aerosols. For non-isotropic aerosol scattering, we explore the measurement bias in the single scattering albedo-asymmetry parameter space, as shown in Figure 2.5. We assume that the aerosol scattering has a Henyey-Greenstein type phase function [Henyey and Greenstein, 1941] with single scattering albedo (SSA) ω_0 and asymmetry parameter g . The AOD is kept constant at 0.1 (in the CO₂ band). We find that the simulated SCDs are always less than the geometric SCD calculated from the true atmospheric profile. This indicates that aerosol scattering reduces the apparent absorption in the normalized radiance, as described in Section 2.3. When calculating X_{CO_2} using Equation (2.1) without taking the wavelength dependence into account, the mean mixing ratio would be over-estimated. At constant AOD, the biases in X_{CO_2} and SCDs depend on both the SSA and the asymmetry parameter. The retrieval bias increases with ω_0 , and decreases with g . By using the delta-Eddington approximation [Wiscombe, 1977], we can get the equivalent isotropic AOD τ_s' and SSA ω' for the forward peaked scattering as shown in Equations (6) – (7) [Goody and Yung, 1989; Liou, 2002].

$$\tau_s' = (1 - f)\tau_s \quad (2.6)$$

$$\omega' = \frac{1 - f}{1 - f\omega} \omega \quad (2.7)$$

where f is the fraction of scattered energy residing in the forward peak. In the delta-Eddington approximation, f is typically taken to be g^2 [Joseph et al., 1976].

Therefore, a more forward-peaked phase function ($g > 0$) leads to smaller aerosol scattering as well as smaller measurement bias.

2.5. Bias correction

With the 2S-ESS model currently in place, it is straightforward to correct the aerosol induced bias in CLARS X_{CO_2} retrievals. Previous studies have demonstrated that the retrieval bias for X_{CO_2} can be greatly mitigated when simple aerosol parameters are incorporated into the retrieval algorithm [Butz *et al.*, 2009; Guerlet *et al.*, 2013]. However, these methods rely on calibrated radiances; for CLARS-FTS, calibration of the absolute radiance is currently unavailable. Using only relative radiances, the retrieval using a full-physics model would face the problem of degeneracy, as presented in Section 2.3. In this study, a fast and effective scaling approach is developed to correct for the bias in X_{CO_2} , as shown in Equation (2.8). The aim is to correct the GFIT retrieval using an empirical relationship between the O_2 SCD and X_{CO_2} retrieval biases gained from a full-physics model, so that we can avoid running computationally expensive retrievals.

$$X_{CO_2} = 0.2095 \frac{SCD_{CO_2}}{SCD_{O_2} \cdot f(b_{O_2})} \quad (2.8)$$

In Equation (2.8), rather than making the assumption that aerosol induced biases in the O_2 and CO_2 SCDs are the same (Equation 2.1), we assume that the biases in the two absorption bands are different. The difference is measured by a correction factor $f(b_{O_2})$ and this factor is only dependent on the bias in O_2 SCD, b_{O_2} (one minus O_2 scaling factor). If Equation (2.1) is a first-order correction, which

mitigates the bias in X_{CO_2} by ratioing CO_2 SCD with O_2 SCD, Equation (2.8) incorporates a second-order correction, which is expected to produce relatively accurate X_{CO_2} values even in the presence of moderate to high aerosol loading.

In Figure 2.6, we calculate the one-to-one relationship between the bias in O_2 SCD, b_{O_2} and the X_{CO_2} correction factor, $f(b_{\text{O}_2})$. The model set-up is the same as in Section 2.4. Climatological aerosol properties in the LA region are used and the viewing geometry is fixed as appropriate for a measurement in West Pasadena. Synthetic data with different AODs are generated. A forward model in which AOD is set to be zero is employed to simulate the retrieval by GFIT. Figure 2.6 (a) shows the retrieval biases in O_2 SCD, CO_2 SCD, and X_{CO_2} as a function of AOD when a simple model like GFIT is applied. A scaling factor of unity corresponds to the true value. The scaling factors for the O_2 SCD (red) and X_{CO_2} (black) can be used to set up an empirical relationship between the O_2 SCD bias and the X_{CO_2} correction factor in Figure 2.6 (b).

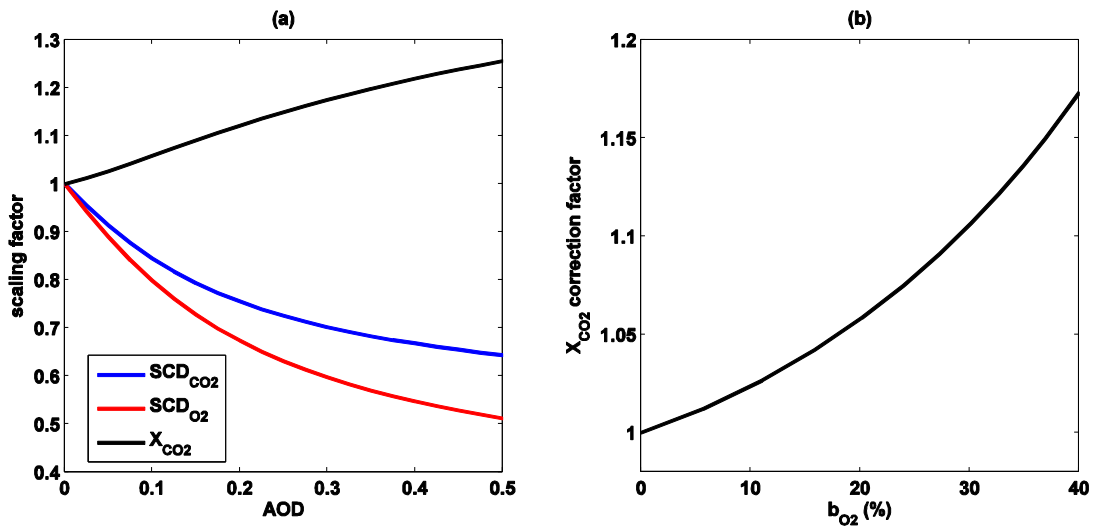


Figure 2.6. (a) Retrieval biases in CO₂ SCD (blue), O₂ SCD (red), and X_{CO₂} (black) caused by different AOD. Retrieval biases are measured by the deficit/excess in scaling factors. In the simulations, each layer in the atmospheric profile is multiplied by the constant scaling factor. Scaling factor = 1 corresponds to the true value. Climatological aerosol parameters in the LA region (Table 1) are used. We use the same viewing geometry as that in Figure 2.5. (b) X_{CO₂} correction factor $f(b_{O_2})$ as a function of O₂ SCD bias.

Using this approach, we can infer the bias in X_{CO₂} from the difference between the measured O₂ SCD and the geometric O₂ SCD. Then, the inferred bias can be used as a scaling factor to correct the X_{CO₂} retrieval result from GFIT. This approach is reasonable because we can get very accurate estimation of the surface pressure from NCEP or ECWMF reanalysis data. The O₂ mixing ratio in the atmosphere is almost constant as 0.2095. It is estimated that the error in the surface pressure *a priori* information for a space-borne mission is below 1 hPa, with 4 hPa as a pessimistic estimate when the uncertainty in topography is considered [O'Dell *et al.*, 2012]. For CLARS-FTS, the target sites are known locations. Therefore, the surface pressure uncertainties should be even smaller than that for a satellite measurement. A surface pressure error of 4 hPa leads to a 0.4% error in the O₂ SCD, which then translates to a 1.6 ppm error in the X_{CO₂} (Equation 1).

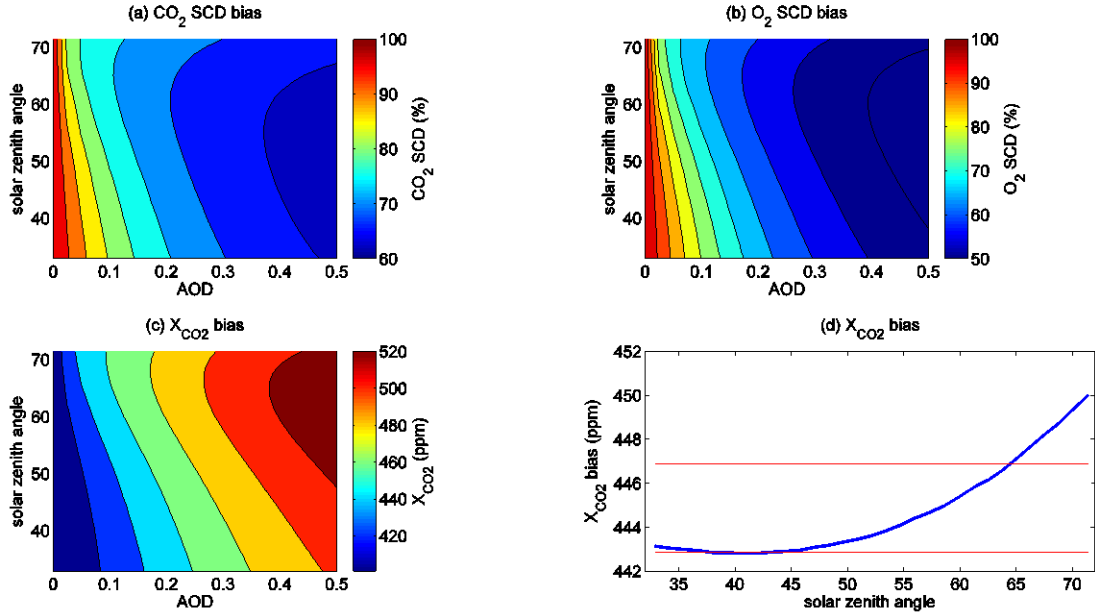


Figure 2.7. Simulation results when aerosol scattering is neglected for: (a) CO₂ SCD, (b) O₂ SCD and (c) X_{CO2}. Combined effect of AOD and viewing geometry is investigated. SCD simulation results are displayed in percentage, 100% corresponds to the true value. The true value of X_{CO2} is 400.8 ppm. Biases are measured as the deviation from the true value. We vary the solar zenith angle from 32.9° (noon) to 72.5° (late afternoon). Relative azimuth angle is also changed correspondingly in the calculation but not shown in figure labels. (d) X_{CO2} for the contour line of $b_{O_2} = 30\%$ (O₂ SCD scaling factor = 0.7). Red lines indicate ± 2 ppm variation.

It is crucial to show that the X_{CO2} correction factor $f(b_{O_2})$ is only a function of the O₂ SCD bias and not influenced by other parameters such as geometry, aerosol phase function, and aerosol SSA. In other words, if we observe a deficit in the measured O₂ SCD, the bias in X_{CO2} can be inferred irrespective of other parameters. Otherwise, $f(b_{O_2})$ would become a multi-variable function and require extensive computation in a multi-dimensional parameter space. In Figure 2.7, we test the combined effect of geometry and AOD on the O₂ SCD, CO₂ SCD and X_{CO2}.

Intuitively, both a larger AOD and a larger SZA would enhance scattering and increase biases in the O_2 and CO_2 SCD retrievals. The scattering angle, which is a function of SZA, AZA, and VZA, also matters if the scattering phase function is not isotropic. To test whether $f(b_{O_2})$ is influenced by geometry, we find the X_{CO_2} values in Figure 2.7(c) corresponding to the 70% O_2 SCD contour in Figure 2.7(b), and plot them as a function of SZA in Figure 2.7(d). If $f(b_{O_2})$ is a function independent of viewing geometry, we would expect to see a straight line, since all the X_{CO_2} scaling factors along the line corresponds to the same O_2 SCD bias ($b_{O_2} = 30\%$). The line in Figure 2.7(d) is not absolutely straight, but the variations are small. The error in X_{CO_2} due to the assumption that $f(b_{O_2})$ is independent of viewing geometry would be within ± 2 ppm, if the solar zenith angle is smaller than 65° (red lines in Figure 2.7d). Note that an O_2 SCD bias of 30% is very large. We rarely observe such a large bias in the CLARS observations even though it has very high sensitivity to aerosol scattering. For a typical CLARS viewing geometry at noon, a 30% O_2 SCD bias indicates a local AOD larger than 0.2 in the $1.61 \mu m$ CO_2 band, or equivalently an AOD larger than 0.4 in the O_2 A-band.

The same method is applied to analyze whether $f(b_{O_2})$ is influenced by the aerosol scattering phase function and SSA, as shown in Figures 2.8 and 2.9. In order to test the sensitivity of the X_{CO_2} correction factor to the aerosol phase function, we employ the Henyey-Greenstein phase function. In Figure 2.8, the combined effects of the phase function asymmetry factor and AOD are tested. The asymmetry parameter g varies from 0 to 1. The SSA is held constant at 0.95 for all simulations. The viewing geometry is fixed as appropriate for an observation in the afternoon,

with $\text{SZA} = 45.2^\circ$, $\text{VZA} = 83.1^\circ$, and $\text{AZA} = 9.7^\circ$. According to the Delta-Eddington approximation, a larger g would reduce the effect of scattering. In Figure 2.8(d), we find that the error in X_{CO_2} due to the assumption that $f(b_{\text{O}_2})$ is independent of the aerosol phase function is within ± 1 ppm, if g is smaller than 0.9.

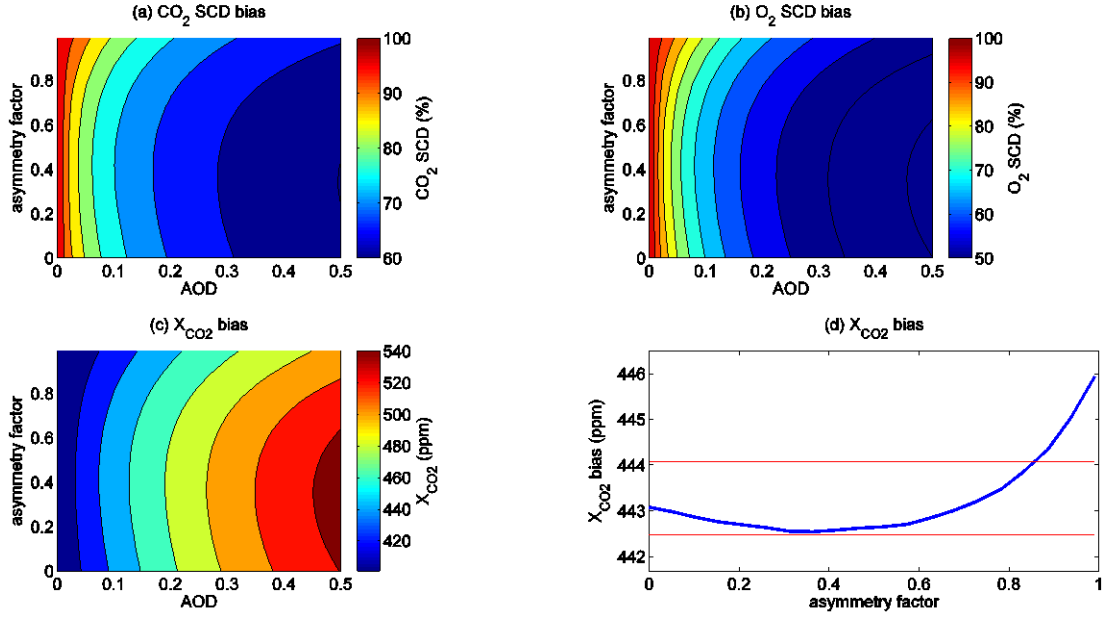


Figure 2.8. Same as Figure 2.7, but for the combined effect of AOD and asymmetry parameter in the scattering phase function. Red lines indicate ± 1 ppm variation.

In Figure 2.9, we fix the asymmetry factor g at 0.75 and explore the sensitivity of $f(b_{\text{O}_2})$ to the aerosol SSA. The same viewing geometry is used in the calculation as that in Figure 2.8. Figure 2.9(d) demonstrates that the error in X_{CO_2} correction due to the assumption that $f(b_{\text{O}_2})$ is independent of aerosol SSA is within ± 1 ppm, if the SSA is larger than 0.2.

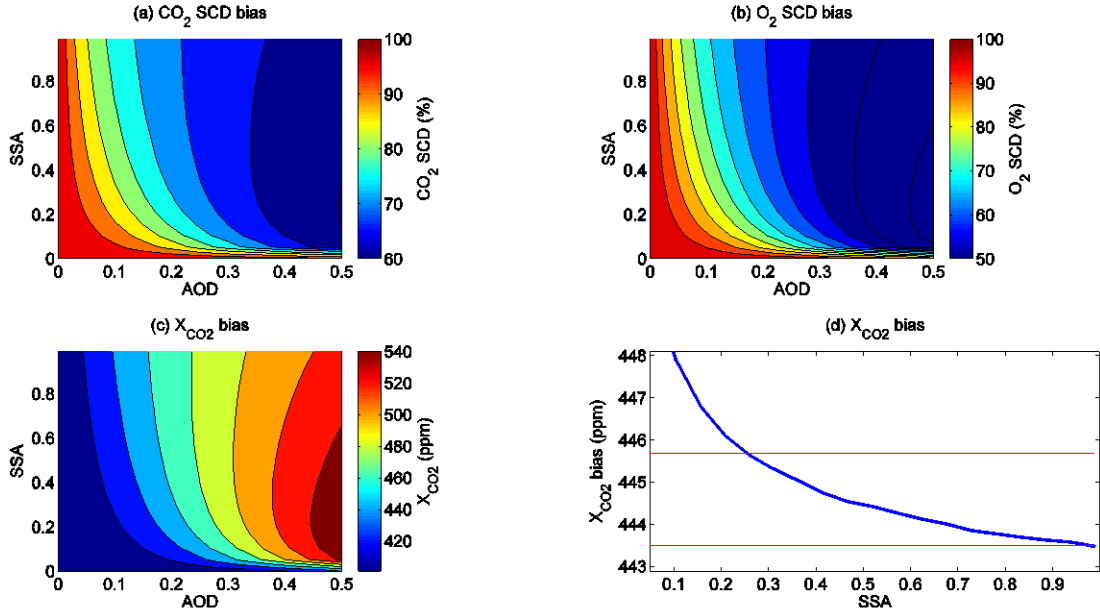


Figure 2.9. Same as Figure 2.7, but for the combined effect of AOD and SSA. Red lines indicate ± 1 ppm variation.

Several factors contribute to the uncertainty of this scaling correction approach. Here we have studied the errors due to uncertainties in surface pressure estimation (σ_{pre}), viewing geometry (σ_{geo}), scattering phase function (σ_g), and aerosol SSA (σ_{SSA}). Assuming that these four effects are independent and uncorrelated, a simple error estimate would be $\sigma = \sqrt{\sigma_{pre}^2 + \sigma_{geo}^2 + \sigma_g^2 + \sigma_{SSA}^2}$, which results in a value of 2.9 ppm. In this study, other parameters such as surface albedo and Angstrom coefficient are assumed to be known from external sources. As we will see in the next section, this approach significantly reduces the aerosol-induced bias in the X_{CO2} product.

2.6. Validation

To test the effectiveness of the bias correction approach, we need to compare the corrected CLARS X_{CO_2} time series against a benchmark. Measurements from CLARS have a long light path through the PBL. Therefore, it is very hard to validate the CLARS X_{CO_2} product using aircraft measurements. TCCON measures the total column average X_{CO_2} from the surface to the top of atmosphere and is often used to validate satellite X_{CO_2} retrievals [Wunch *et al.*, 2011]. The TCCON station at JPL is very close to the CLARS West Pasadena target site in both the horizontal and vertical directions. We employ the JPL TCCON data as the ground truth to validate the CLARS X_{CO_2} measurements. However, the comparison is not straightforward. CLARS X_{CO_2} measurements have a much larger contribution from the PBL than TCCON or a typical satellite (Figure 2.1). In megacities with large CO_2 emissions, X_{CO_2} in the PBL is often higher than that in the free troposphere. Therefore, we expect the CLARS X_{CO_2} measurements to be higher than those from TCCON. Fortunately, we also have CLARS Spectralon measurements to constrain the X_{CO_2} in the free troposphere. The CLARS Spectralon viewing mode takes direct sun measurements similar to TCCON. For most of the daytime, the PBL top is below the CLARS site and the spectralon measurements are not influenced by aerosol scattering [Newman *et al.*, 2013].

We use a simple two-box model to calculate the CO_2 mixing ratio along the CLARS West Pasadena light path, as shown in Figure 2.1. We assume that the CO_2 mixing ratio is X_0 and $X_0 + \Delta X$ in the free troposphere and the PBL, respectively. Pressures at the surface, the top of the PBL, and the CLARS instrument are P_0 , $P_0 -$

ΔP , and P_1 , respectively. Using this simple model, the JPL TCCON station measurements (TCC), CLARS Spectralon measurements (SPC), and estimated CLARS West Pasadena measurements (WP) can be calculated using Equation (2.9) – (2.11).

$$SPC = X_0 \quad (2.9)$$

$$TCC = X_0 + \Delta P \Delta X / P_0 \quad (2.10)$$

$$WP = X_0 + \frac{\Delta P \Delta X [1 / \cos(SZA) + 1 / \cos(VZA)]}{P_0 / \cos(SZA) + (P_0 - P_1) / \cos(VZA)} \quad (2.11)$$

If the viewing geometries of both TCCON and CLARS West Pasadena measurements are known, we can solve for WP and calculate the estimated average CO_2 mixing ratio along the CLARS light path in West Pasadena, as shown in Equation (2.12):

$$WP = \frac{(TCC - SPC) \cdot [P_0 / \cos(SZA) + P_0 / \cos(VZA)]}{P_0 / \cos(SZA) + (P_0 - P_1) / \cos(VZA)} + SPC \quad (2.12)$$

This method is not sensitive to the PBL height so long as the PBL is below the CLARS site. There are several assumptions made here. First, we assume that the PBL height is uniform in both the incoming solar and outgoing viewing directions. Second, the X_{CO_2} in the PBL and the free troposphere is well mixed and horizontally uniform. We also neglect the spatial differences between the TCCON JPL station and the CLARS West Pasadena target site.

In Figure 2.10, CLARS and TCCON measurements on March 23, 2013 are shown. In the left panel, TCCON X_{CO_2} measurements are shown in red and CLARS Spectralon X_{CO_2} measurements are shown in green. The expected average X_{CO_2}

along the CLARS light path in West Pasadena (black) is calculated according to Equation (2.12) using both TCCON and CLARS Spectralon measurements. The blue curve shows the CLARS operational X_{CO_2} product without any correction. It is clear that in the afternoon, CLARS X_{CO_2} retrievals show a high bias of up to 20 ppm due to aerosol scattering, consistent with the analysis in Figure 2.5.

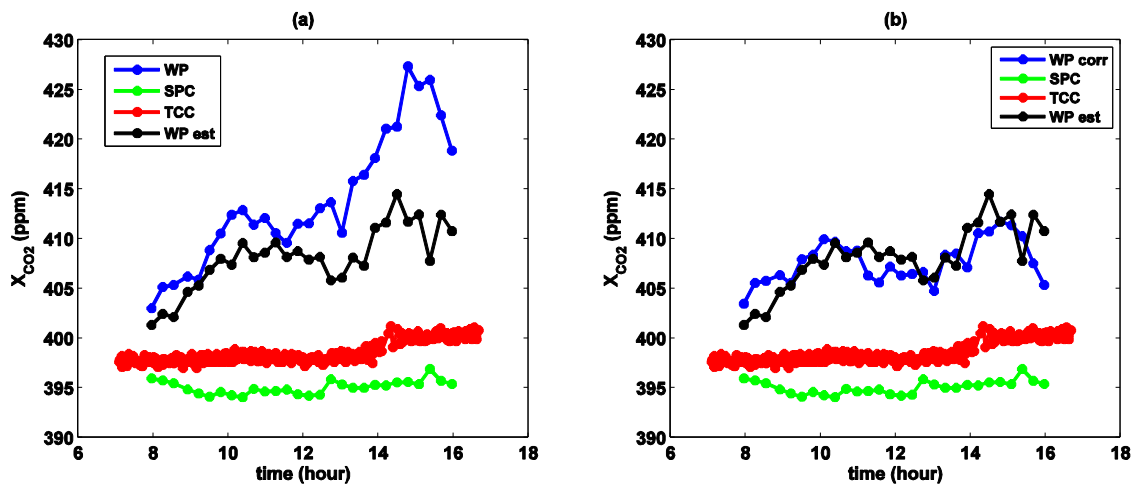


Figure 2.10. Validation of CLARS West Pasadena measurements. Data on March 23, 2013 are shown. Green curves represent the CLARS Spectralon X_{CO_2} data (SPC). Red curves represent the JPL TCCON station X_{CO_2} data (TCC). Black curves represent the estimation of X_{CO_2} along the CLARS viewing light path at West Pasadena (WP est). In Panel (a), the blue curve represents the CLARS operational X_{CO_2} product in West Pasadena retrieved by GFIT (WP). In Panel (b), the blue curve represents the corrected CLARS X_{CO_2} product using our proposed approach (WP corr).

In the right panel of Figure 2.10, the green, red, and black curves are the same as those in the left panel, representing CLARS Spectralon, TCCON, and estimated CLARS West Pasadena measurements. The blue curve is the corrected CLARS West Pasadena measurement using the scaling approach proposed above. We first

determine the O_2 SCD bias from the difference between the geometric and measured O_2 SCDs (e.g., Figure 2.2). Then, the corresponding X_{CO_2} correction factor $f(b_{O_2})$ can be found from Figure 2.6(b). We finally divide the GFIT operational X_{CO_2} product (blue curve in the left panel) by this correction factor and get the corrected X_{CO_2} measurements (blue curve in the right panel). The aerosol induced bias in X_{CO_2} is significantly reduced by making the correction. The root mean square (RMS) of the discrepancies between the black and blue curves in Figure 2.10 (b) is 2.4 ppm, which is below our error estimate. As shown in Figure 2.10, CLARS-FTS has excellent sensitivity to boundary layer X_{CO_2} enhancement, which makes it particularly useful to study emissions in a megacity. The estimated error for this proposed correction approach is larger than that for a satellite-based measurement (e.g. OCO-2 [O'Dell *et al.*, 2012]), mainly because CLARS-FTS has high sensitivity to aerosol scattering and we are studying hazy scenarios in a megacity. However, the precision is good enough for analyzing the temporal and spatial variability of X_{CO_2} in the LA basin.

CLARS measurements on other hazy days show similar features as Figure 2.10. When aerosol scattering is neglected, the X_{CO_2} retrieval typically shows a high bias. The bias can be significantly reduced when we apply the correction approach based on the O_2 SCD. In Figure 2.11, we test all available CLARS West Pasadena measurements in 2013 when concurrent JPL TCCON measurements are available. The RMS of discrepancies between the X_{CO_2} measurements and the estimates (Equation 2.12) is reduced from 9.1 ppm to 3.4 ppm by the proposed correction approach. The correlation coefficient between the X_{CO_2} measurements and

estimates also rises from 0.56 to 0.80 as a result of the correction. The approach proposed in this study only aims to correct the X_{CO_2} retrieval bias caused by aerosol scattering. There are other factors that potentially contribute to the discrepancy between the corrected CLARS measurements and the estimates using Equation (2.12). For example, the assumptions that the PBL height is uniform and that CO_2 is well mixed in the PBL may not hold in some cases.

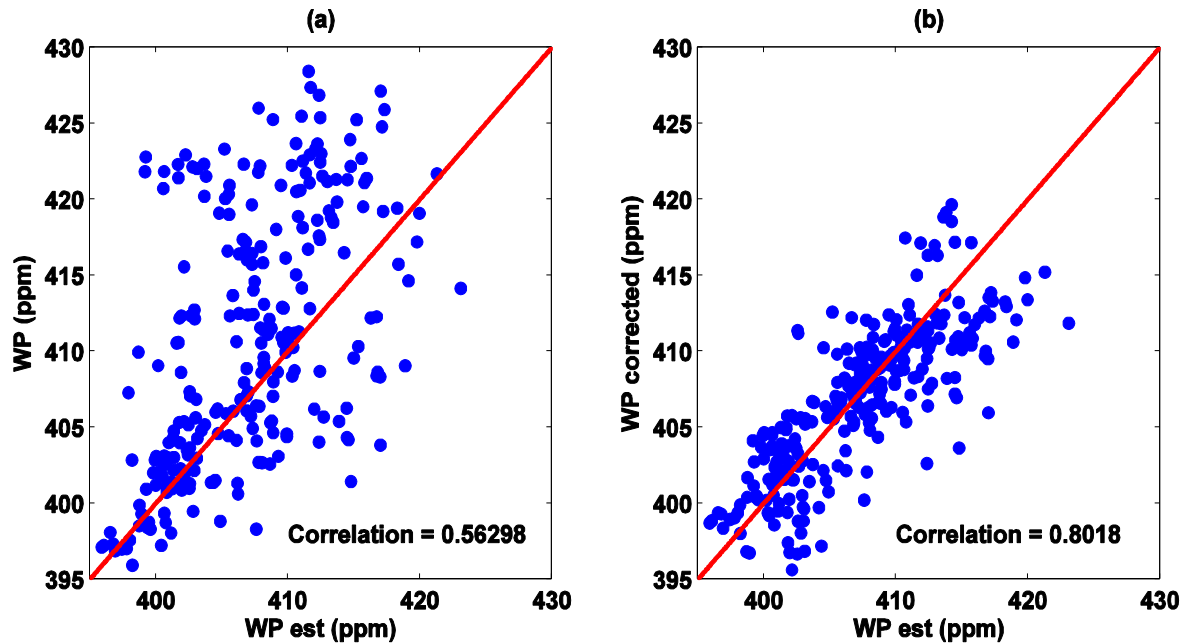


Figure 2.11. Scatter plot of CLARS West Pasadena X_{CO_2} measurements against the estimates (WP est) based on Equation (2.12). (a) CLARS measurements (WP) retrieved by GFIT, which totally neglects aerosol scattering. (b) Corrected measurements (WP corrected) using our proposed method. The red line in each panel shows the 1:1 relationship. Without correction, the correlation coefficient between the CLARS West Pasadena measurements and the estimates based on Equation (2.12) is 0.56. After the correction, the correlation coefficient rises to 0.80. The displayed data are from 9 separate days of observations and include 274 separate data points.

2.7. Discussions and conclusions

Assuming that the aerosols are evenly distributed in the PBL, the CLARS-FTS retrieved SCD shows a low bias regardless of the value of aerosol SSA and phase function asymmetry parameter. An examination of CLARS-FTS measurements (similar to Figure 2.2) on other hazy days also confirms that the retrievals of CO₂ and O₂ SCDs are less than the geometric estimates without exception. This is mainly due to the unique observation geometry of the CLARS-FTS instrument. The CLARS site is very low in altitude. Only the aerosols within the PBL strongly influence the observed reflected spectral radiance. For a typical satellite viewing geometry, if the surface is bright and the aerosol/cloud layer is high, scattering could also enhance photon path length, resulting in an increased apparent absorption.

Aerosol scattering has wavelength dependence. Therefore, ratioing CO₂ and O₂ SCDs cannot totally cancel the bias in the X_{CO2} product. The X_{CO2} bias can be mitigated by simply filtering the data based on the criterion that O₂ SCD bias < 10%, as demonstrated in *Wong et al.* [2015].

We propose an effective and fast approach to correct the aerosol induced bias in the X_{CO2} retrieval using non-calibrated reflected solar radiance. The approach is potentially applicable to other ground based instruments dedicated to measuring greenhouse gas abundances. X_{CO2} could first be retrieved using a simple and fast model, such as GFIT, which allows for non-calibrated radiance but does not account for aerosol scattering. The bias in the X_{CO2} product caused by aerosol scattering can be reduced based on the difference between the measured and geometric O₂ SCDs.

This approach offers a much higher accuracy than a simple ratioing between the O₂ and CO₂ SCDs. Since GFIT is much simpler and faster than most of the full-physics models, this approach is numerically efficient and particularly applicable to massive data processing when computational resources are limited.

The correction accuracy could be further improved by incorporating another parameter, other than the bias in the O₂ SCD, into the empirical relationship. In this study, we use a fixed Angstrom coefficient to constrain the wavelength dependence of AOD between the 1.61 μm CO₂ band and the 1.27 μm O₂ band. This not a serious problem in this study since the CO₂ and O₂ bands are close to each other. However, the error caused by an inaccurate Angstrom coefficient would increase if the O₂ A band (0.76 μm) were used in the retrieval. For a typical CLARS-FTS measurement with AOD = 0.1 in the CO₂ absorption band, a ± 0.1 variation in the Angstrom coefficient results in a ± 0.0029 variation in the O₂ absorption band AOD, which translates into 2 ppm bias in X_{CO₂}. In principle, we can set up a two-variable empirical function $f(b_{O_2}, \kappa)$ to correct for the bias in X_{CO₂}, where κ is the AOD Angstrom coefficient. This would require additional information on the AOD wavelength dependence. Surface albedo is another important parameter as incorrect albedos in the CO₂ and O₂ absorption bands could potentially lead to biases in the X_{CO₂} products. For CLARS instrument, surface albedo can be measured on a clear day with reference to the spectra from the Spectralon.

The CLARS mountaintop remote sensing observations of greenhouse gases in an urban source region provide a heretofore unavailable dataset to study the effects of aerosols on high-precision trace gas retrievals. Since these data are diurnally

resolved over a wide range of solar zenith and viewing angles and aerosol loadings, they provide for a critical comparison between the retrieved SCD daily variations from CLARS-FTS measurements and the model simulations constrained by AERONET data. The framework developed here provides a means to compare the CLARS results with reference data from simultaneous TCCON observations, which are relatively immune to aerosol extinction.

There are potential applications of CLARS-FTS measurements for the OCO-3 CO₂ mission [Eldering *et al.*, 2014]. OCO-3 employs an agile pointing system, thus permitting a city mode, which maps an area approximately 60 km × 60 km at high resolution (~5.5 km in nadir view from 400 km altitude). This observing mode, combined with the low-inclination orbit of the International Space Station (ISS), which precesses in local time, is ideal for detecting and quantifying the spatial variability of fossil fuel emissions in rapidly developing urban centers. The measurements from CLARS-FTS provide the capability of spatially mapping the GHGs in the LA basin, whose emissions vary in complex temporal/spatial multimodal cycles. This unique spatial mapping capability of CLARS-FTS measurements, which helps in validating OCO-3 measurements under urban environments, is not available from the existing TCCON measurements. In addition, it is possible to generalize our work to include other species such as CH₄ and CO. Our results can also be used to improve the retrieval algorithm for the ESA TROPOspheric Monitoring Instrument (TROPOMI) mission [Veefkind *et al.*, 2012].

Appendix 2.1: Two-stream analytic model

A.2.1.1. Influence of aerosols on radiance

We solve a simplified radiative transfer equation without the source term as shown in equation (2.A1) to explain the change of radiance due to aerosols [Goody and Yung, 1989; Liou, 2002]. We assume that the scattering is isotropic and the single scattering albedo ω_0 is a constant. In this equation I is the radiance, τ is the optical depth and $\mu=1/\cos(\theta)$, where θ is the viewing zenith angle or the SZA. This approximation is accurate only to the first order. We neglect the term associated with the incoming solar irradiance and assume that it is the same as the isotropic diffusive flux at the top of the atmosphere.

$$\mu \frac{\partial I(\tau, \mu)}{\partial \tau} = I(\tau, \mu) - \frac{1}{2} \omega_0 \int_{-1}^1 I(\tau, \mu) d\mu \quad (2.A1)$$

Separating upward and downward streams using two-stream approximation as

$$\bar{\mu} \frac{dI^+(\tau, \bar{\mu})}{d\tau} = I^+(\tau, \bar{\mu}) - \frac{1}{2} \omega_0 [I^+(\tau, \bar{\mu}) + I^-(\tau, -\bar{\mu})] \quad (2.A2)$$

$$-\bar{\mu} \frac{dI^-(\tau, -\bar{\mu})}{d\tau} = I^-(\tau, -\bar{\mu}) - \frac{1}{2} \omega_0 [I^+(\tau, \bar{\mu}) + I^-(\tau, -\bar{\mu})] \quad (2.A3)$$

we can solve for general solutions as below, where $I^+(\tau) = I^+(\tau, \bar{\mu})$, $I^-(\tau) = I^-(\tau, \bar{\mu})$.

$$I^+(\tau) = (1 - \bar{\mu}\rho)c_1 e^{-\rho\tau} + (1 + \bar{\mu}\rho)c_2 e^{\rho\tau} \quad (2.A4)$$

$$I^-(\tau) = (1 + \bar{\mu}\rho)c_1 e^{-\rho\tau} + (1 - \bar{\mu}\rho)c_2 e^{\rho\tau} \quad (2.A5)$$

$$\rho^2 = \frac{1 - \omega_0}{\bar{\mu}^2} \quad (2.A6)$$

$$\bar{\mu} = \frac{1}{\sqrt{3}} \quad (2.A7)$$

Applying the boundary conditions to account for the reflection at the surface, where α is the surface albedo and F is the incoming solar flux,

$$(1 + \bar{\mu}\rho)c_1 + (1 - \bar{\mu}\rho)c_2 = \frac{1}{2\pi} F \quad (2.A8)$$

$$(1 - \bar{\mu}\rho)c_1 e^{-\rho\tau_1} + (1 + \bar{\mu}\rho)c_2 e^{\rho\tau_1} = \alpha[(1 + \bar{\mu}\rho)c_1 e^{-\rho\tau_1} + (1 - \bar{\mu}\rho)c_2 e^{\rho\tau_1}] \quad (2.A9)$$

we can get the two-stream general solution with surface albedo at arbitrary optical depth

$$I^+(\tau) = \frac{1}{2\pi} F \frac{[\omega_0 - \alpha(1 - \bar{\mu}\rho)^2]e^{\rho(\tau_1 - \tau)} - [\omega_0 - \alpha(1 + \bar{\mu}\rho)^2]e^{-\rho(\tau_1 - \tau)}}{[(1 + \bar{\mu}\rho)^2 - \alpha\omega_0]e^{\rho\tau_1} - [(1 - \bar{\mu}\rho)^2 - \alpha\omega_0]e^{-\rho\tau_1}} \quad (2.A10)$$

$$I^-(\tau) = \frac{1}{2\pi} F \frac{[(1 + \bar{\mu}\rho)^2 - \alpha\omega_0]e^{\rho(\tau_1 - \tau)} - [(1 - \bar{\mu}\rho)^2 - \alpha\omega_0]e^{-\rho(\tau_1 - \tau)}}{[(1 + \bar{\mu}\rho)^2 - \alpha\omega_0]e^{\rho\tau_1} - [(1 - \bar{\mu}\rho)^2 - \alpha\omega_0]e^{-\rho\tau_1}} \quad (2.A11)$$

At the top and bottom, emergent radiances are shown by equation (2.A13)-(2.A14).

$$I^+(0) = \frac{1}{2\pi} F \frac{[\omega_0 - \alpha(1 - \bar{\mu}\rho)^2]e^{\rho\tau_1} - [\omega_0 - \alpha(1 + \bar{\mu}\rho)^2]e^{-\rho\tau_1}}{[(1 + \bar{\mu}\rho)^2 - \alpha\omega_0]e^{\rho\tau_1} - [(1 - \bar{\mu}\rho)^2 - \alpha\omega_0]e^{-\rho\tau_1}} \quad (2.A13)$$

$$I^-(\tau_1) = \frac{2\bar{\mu}\rho F}{\pi} \frac{1}{[(1 + \bar{\mu}\rho)^2 - \alpha\omega_0]e^{\rho\tau_1} - [(1 - \bar{\mu}\rho)^2 - \alpha\omega_0]e^{-\rho\tau_1}} \quad (2.A14)$$

The non-dimensional value of reflectance is calculated in equation (2.A15).

$$R(\tau_1, \omega_0) = \frac{[\omega_0 - \alpha(1 - \bar{\mu}\rho)^2]e^{\rho\tau_1} - [\omega_0 - \alpha(1 + \bar{\mu}\rho)^2]e^{-\rho\tau_1}}{[(1 + \bar{\mu}\rho)^2 - \alpha\omega_0]e^{\rho\tau_1} - [(1 - \bar{\mu}\rho)^2 - \alpha\omega_0]e^{-\rho\tau_1}} \quad (2.A15)$$

A.2.1.2. One-line spectra

Only pressure broadening is considered in this model as Doppler and natural broadenings are weak in the troposphere where most of the absorption occurs [Goody and Yung, 1989]. The atmosphere is divided into two layers: a free troposphere with absorption only and a PBL with absorption and scattering. We define the pressure at the top of PBL to be P_1 . In this model, P_1 is defined to be 800 hPa.

The absorption coefficient of a Lorentzian absorption line shape is

$$k = S \frac{\alpha_L}{\pi} \frac{1}{\alpha_L^2 + (\nu - \nu_0)^2} \quad (2.A16)$$

where $\alpha_L = \alpha_L^0(p / p_0)$ is half-width of the line at the half-maximum [Liou, 2002], p is the pressure and α_L^0 is the line width at the reference pressure p_0 . The optical depth of the free troposphere is given by

$$\tau_1 = \tau_{1a} = \frac{S\chi}{\pi mg} \int_0^{P_1} \frac{Ap}{(Ap)^2 + (\nu - \nu_0)^2} dp = \frac{S\chi}{2\pi mgA} \ln \frac{P_1^2 + [(\nu - \nu_0) / A]^2}{[(\nu - \nu_0) / A]^2} \quad (2.A17)$$

where S is the line strength constant, $A = \alpha_L / p = \alpha_L^0 / p_0$. The two constants A and S can be obtained from the HITRAN database [Rothman et al., 2008]. In this model, for the CO_2 absorption line $\nu_0 = 6243.9 \text{ cm}^{-1}$, $S = 1.52 \times 10^{-23} \text{ cm}$, $A = 7.2 \times 10^{-7} \text{ cm}^{-1} \text{ Pa}^{-1}$. χ is the volume mixing ratio of the absorbing gas (CO_2). We set χ to be 400 ppm for CO_2 . In the equation $m = 4.8 \times 10^{-26} \text{ kg}$ is the mean molecular weight of air, g is 9.8 m/s^2 . Note that $mg = 4.7 \times 10^{-21} \text{ cm}^2 \text{ Pa}$ is a constant. Transmittance of the free troposphere is

$$T_1 = e^{-\tau_1} \quad (2.A18)$$

In the PBL, the total optical depth is

$$\tau_{2a} = \frac{S\chi}{\pi mg} \int_{P_1}^{P_s} \frac{Ap}{(Ap)^2 + (\nu - \nu_0)^2} dp = \frac{S\chi}{2\pi mgA} \ln \frac{P_s^2 + [(\nu - \nu_0)/A]^2}{P_1^2 + [(\nu - \nu_0)/A]^2} \quad (2.A19)$$

$$\tau_2 = \tau_{2a} + \tau_s \quad (2.A20)$$

$$\gamma = \frac{\tau_s}{\tau_{2a} + \tau_s} = \frac{\tau_s}{\tau_2} \quad (2.A21)$$

where $P_s = 1030$ hPa is the surface pressure. According to equation (2.A17), at the center of the absorption line where $\nu = \nu_0$, we have a singular point with infinite absorption optical depth. In the calculation, most of the channels are away from the singular point ($|\nu - \nu_0| > 0.001 \text{ cm}^{-1}$) where Lorentzian line shape is still a good approximation. This problem can be avoided in a more realistic line shape. The parameter γ is defined to be the ratio of AOD in the PBL to the total optical depth in this layer. We can modify the radiative transfer equation as

$$\mu \frac{dI(\tau, \mu)}{d\tau} = I(\tau, \mu) - \frac{1}{2} \omega_0 \gamma \int_{-1}^1 I(\tau, \mu) d\mu \quad (2.A22)$$

Repeating the calculations of the two-stream approximation, we can get the reflectance of the PBL as equation (2.A23).

$$R_2 = \frac{[\omega_0 \gamma - \alpha(1 - \bar{\mu}\rho)^2]e^{\rho\tau_2} - [\omega_0 \gamma - \alpha(1 + \bar{\mu}\rho)^2]e^{-\rho\tau_2}}{[(1 + \bar{\mu}\rho)^2 - \alpha\omega_0 \gamma]e^{\rho\tau_2} - [(1 - \bar{\mu}\rho)^2 - \alpha\omega_0 \gamma]e^{-\rho\tau_2}} \quad (2.A23)$$

Finally, what we observe as the reflectance at the level of CLARS instrument is

$$R = T_1 \cdot R_2 = e^{-\tau_1} \cdot \frac{[\omega_0 \gamma - \alpha(1 - \bar{\mu}\rho)^2]e^{\rho\tau_2} - [\omega_0 \gamma - \alpha(1 + \bar{\mu}\rho)^2]e^{-\rho\tau_2}}{[(1 + \bar{\mu}\rho)^2 - \alpha\omega_0 \gamma]e^{\rho\tau_2} - [(1 - \bar{\mu}\rho)^2 - \alpha\omega_0 \gamma]e^{-\rho\tau_2}} \quad (2.A24)$$

where τ_1 , τ_2 and γ are wavelength dependent. In this study, both the solar zenith angle and the viewing zenith angle are set to be zero. To incorporate the variation of solar zenith angle θ , we assume in each layer the optical depth

$$\tau_i(\theta) = \frac{\tau_i(0)}{\cos(\theta)} \quad (2.A25)$$

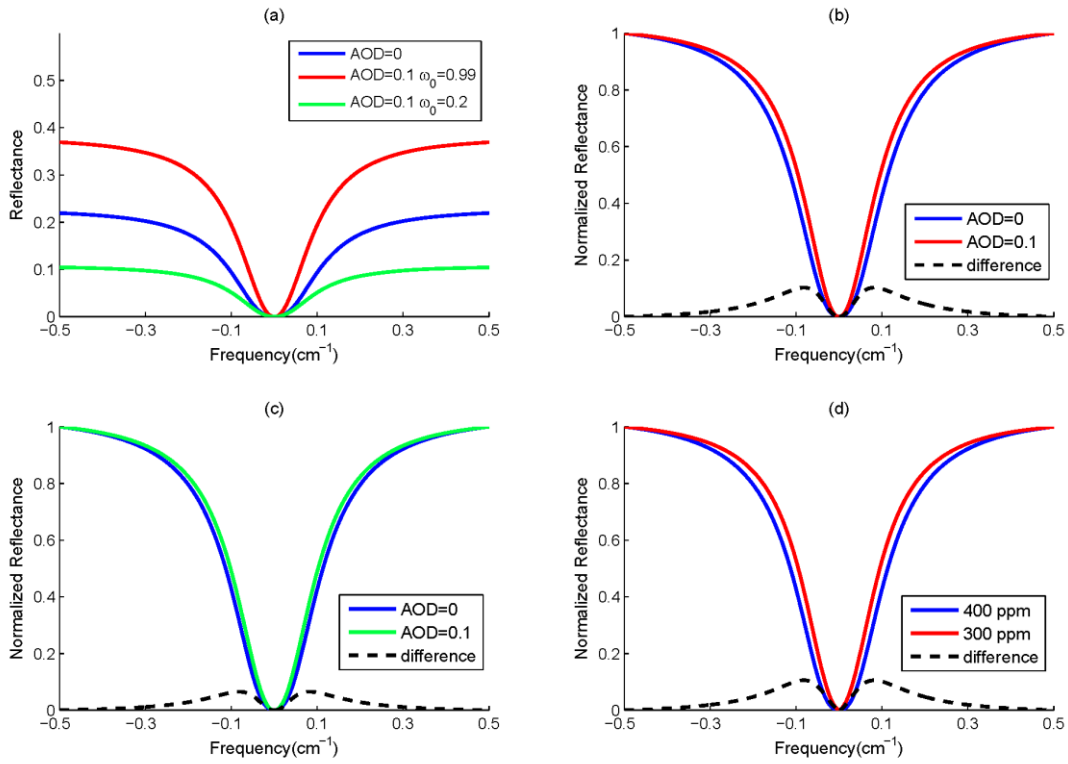


Figure 2.A1. One-line spectra simulated by the analytic model for a CO₂ absorption line. (a) Absolute reflectance with different AOD and ω_0 in the PBL. (b) Normalized reflectance with different AOD in the PBL, $\omega_0=0.99$. (c) Same as (b), $\omega_0=0.2$. (d) Normalized reflectance with different CO₂ concentrations, AOD = 0. The central frequency $\nu_0 = 6243.9 \text{ cm}^{-1}$ has been subtracted. Black dashed line shows the difference between the two spectra.

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X_{CO₂} RETRIEVAL ERROR OVER DESERTS NEAR CRITICAL SURFACE ALBEDO

3.1. Introduction

The Orbiting Carbon Observatory-2 mission (OCO-2) was launched in July 2014 to measure the concentration of CO₂ accurately from space. OCO-2 was designed to map the global column-averaged CO₂ dry-air mixing ratio (X_{CO₂}) in order to characterize CO₂ sources and sinks on regional scales [Kuang *et al.*, 2002; Crisp *et al.*, 2004]. The OCO-2 instrument features high precision, small footprint, and global coverage. It is ideal for studying the global carbon cycle. Since CO₂ is well mixed in the atmosphere, CO₂ flux inversion typically requires retrieval accuracy up to 1 ppm [Miller *et al.*, 2007]. Such data could significantly reduce the uncertainties in the regional CO₂ flux estimation [Rayner and Brien, 2001]. However, any X_{CO₂} retrieval errors larger than the accuracy requirement would lead to significant biases in the flux inversion.

Aerosol scattering is often considered the major source of error in the remote sensing of greenhouse gases [Aben *et al.*, 2007]. Scattering in the atmosphere could change the photon path distribution, thus altering the apparent absorption of the target trace gas [Oshchepkov *et al.*, 2008]. There are many recent studies on the CO₂ retrieval errors related to aerosol scattering. For example, Houweling *et al.* [2005] examined the Scanning Imaging Absorption Spectrometer for Atmospheric

Chartography (SCIAMACHY) CO₂ retrieval and found a bias of up to 10% over the Sahara Desert. *Uchino et al.* [2012] compared the Greenhouse Gases Observing Satellite (GOSAT) retrievals with Total Carbon Column Observing Network (TCCON) and lidar measurements over Tsukuba, and identified high-altitude aerosols and thin cirrus clouds as the major sources of error.

The surface albedo has often the most significant effect on the reflected radiance observed at top of atmosphere even in the presence of aerosol scattering. The concept of critical surface albedo (α_c) was first proposed by *Fraser and Kaufman* [1985]. Intuitively, increasing AOD could either increase or decrease the top of atmosphere reflectance as the aerosols appear to be brighter (such as sulfate) or darker (such as soot) than the surface. The critical surface albedo is defined as the albedo where the derivative of the top of atmosphere radiance with respect to AOD is equal to zero in the continuum [*Seidel and Popp*, 2012]. In the continuum, clear sky gaseous absorption optical depth is zero. A surface with albedo close to α_c could cause large errors in the retrieval of AOD from space, since the radiance measurement loses sensitivity to the variation of AOD. The concept of critical surface albedo has been extensively applied in the retrieval of surface and aerosol properties [e.g. *Banks et al.*, 2013; *Sayers et al.*, 2013]. However, it is less well known in the field of greenhouse gas retrieval. While aerosols are hard to detect over a surface with albedo close to α_c , they can change the photon path length and therefore influence the retrieval of greenhouse gas column abundances.

The aim of this paper is to test the hypothesis that the OCO-2 X_{CO2} retrieval errors over desert regions are due to the albedo being close to the critical surface

albedo. In Section 3.2, we examine the OCO-2 version 7 data to identify regions with large X_{CO_2} retrieval errors. In Section 3.3, we employ a two-stream-exact single scattering (2S-ESS) radiative transfer model to study the physical mechanism of the X_{CO_2} retrieval errors over a surface with albedo close to α_c . A discussion of our results follows in Section 3.4.

3.2. X_{CO_2} retrieval errors over deserts

In this section, we study the OCO-2 retrieval error over desert regions where surface albedos are high. Online Version 7r data are used in the study (<http://oco.jpl.nasa.gov/science/ocodatacenter/>). In the OCO-2 dataset, retrieval quality is labeled with two ‘flags’: 0. 'Passed internal quality check'; 1. 'Failed internal quality check'. In Figure 3.1, we plot all the X_{CO_2} retrievals in April 2015. Currently, OCO-2 gathers as many as 72,000 spectra on the sunlit side of any single orbit, or 24 per second [Mandrake *et al.*, 2014]. Monthly data are enough for global coverage. By comparing Figure 3.1a and Figure 3.1b, we find that most of the data points that fail to pass the quality check are located over desert regions such as the Sahara Desert and Central Asia. X_{CO_2} retrievals over these regions show significant low biases compared with surrounding areas. Since the deserts are unlikely to be a significant sink of CO_2 , X_{CO_2} retrieval bias over these regions appears to be an artifact.

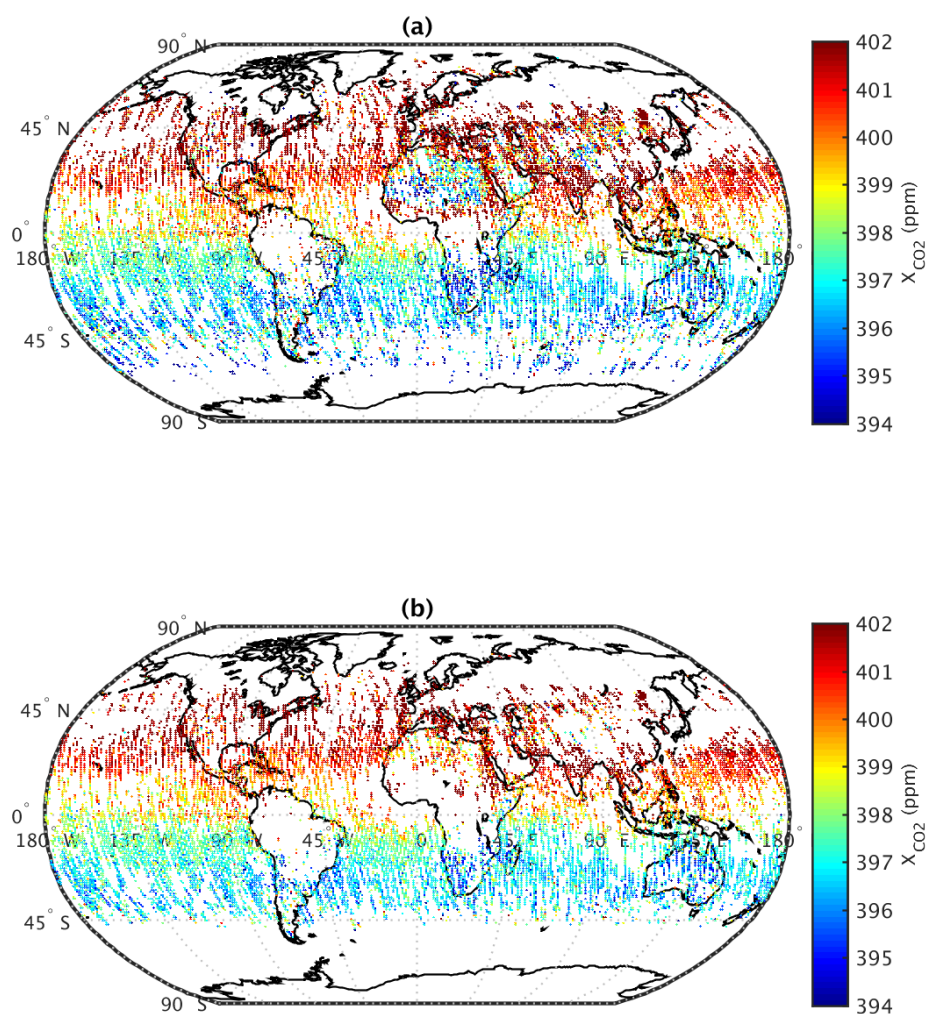


Figure 3.1 Global map of OCO-2 XCO₂ retrieval in April 2015. (a) All the data points are displayed. In OCO-2 retrievals, data qualities are labeled with 'flag' 0 and 1: 0. 'Passed internal quality check'; 1. 'Failed internal quality check'. (b) Only the data points labeled with 'flag 0' are displayed.

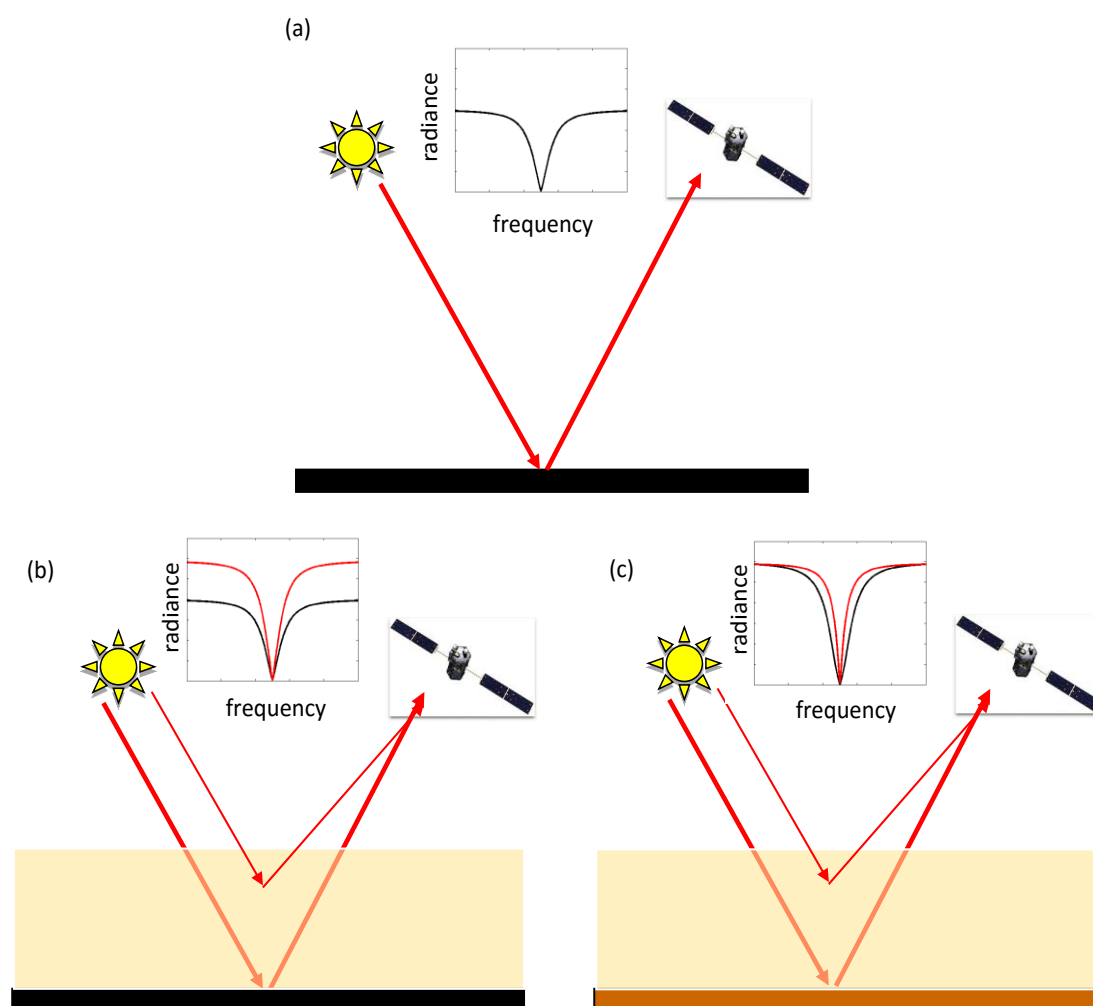


Figure 3.2 Schematic figures of reflection and scattering over surfaces with difference albedos. The small window at the top of each panel shows the one-line absorption spectra. Black spectra represent the reflection in a clear scenario over a dark surface. Red spectra represent the reflection and scattering in a hazy scenario. (a) Clear scenario, AOD = 0. (b) Scattering over a dark surface. (c) Scattering over a surface with albedo close to α_c .

We will examine the hypothesis that the retrieval errors over desert regions are due to the albedo being close to the critical surface albedo. The concept of critical surface albedo is explained in Figure 3.2. The three panels represent (a) clear scenario, (b) scattering over a low albedo surface, and (c) scattering over a surface with albedo close to α_c . Schematic figures of one-line spectra are also shown in each panel. Intuitively, bright aerosols over a dark surface would increase the radiance in the continuum, as shown in Figure 3.2b. The presence of such aerosols is very easy to detect from the shift of the continuum radiance. However, over a critical surface albedo region, as shown in Figure 3.2c, increasing the AOD does not change the absolute radiance in the continuum. Aerosols can cause changes in the photon path length through the atmosphere, thereby modifying the apparent absorption. The net result is the filling-in of the absorption lines, while the continuum remains the same. This effect is the same for all absorption lines. Quantitatively, it can be derived from our analytic model presented in Chapter 2. We will demonstrate in the next section that over such a surface with albedo close to α_c , the effect of changing AOD is almost the same as that caused by changing absorbing gas column abundance. Over such regions, the interference between aerosol scattering and CO₂ absorption will cause degeneracy in the retrieval of AOD and CO₂, leading to a large error in the X_{CO_2} retrieval.

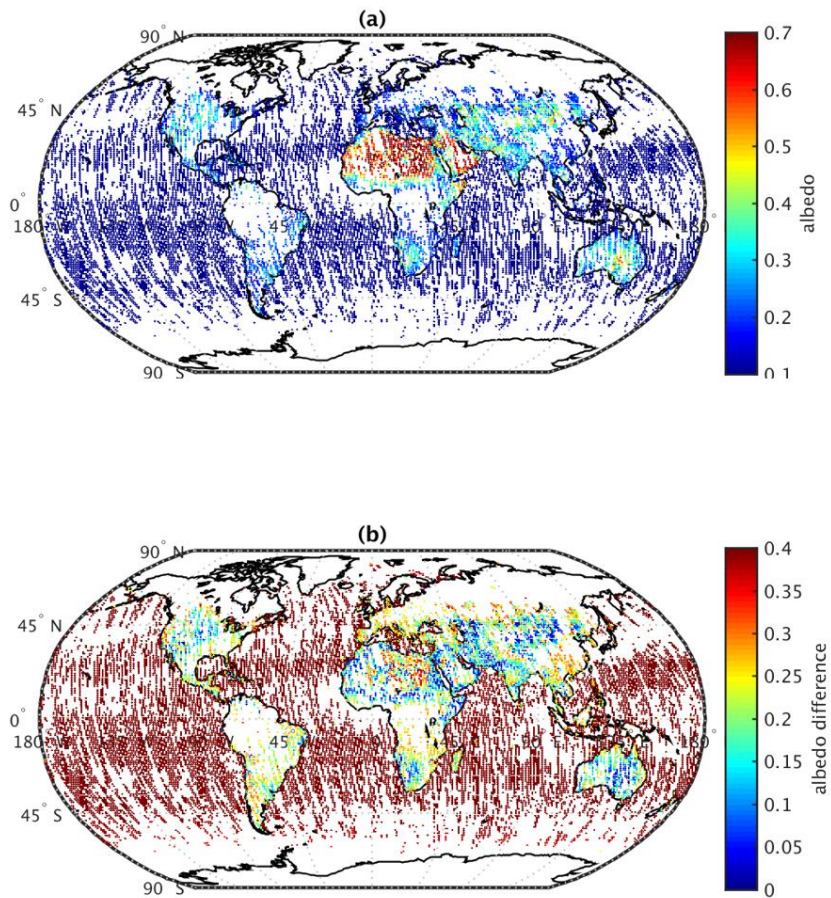


Figure 3.3 (a) Global map of the retrieved surface albedo in the 1.6 μm weak CO_2 band in April 2015. (b) Difference between the retrieved surface albedo and the critical surface albedo of 0.46. Differences are displayed in absolute values. We assume that the aerosol has mineral dust properties with $\text{SSA} = 0.94$. The aerosol SSA is defined as the ratio between the scattering optical depth and the total extinction optical depth. In Section 3.3, we use the same surface albedo for all the absorption bands in the simulations.

To confirm our hypothesis that the retrieval errors are caused by the surface albedo being close to the critical value, we examine the surface albedo in Figure 3.3. Figure 3.3a shows the retrieved surface albedo in the CO₂ 1.6 μm weak band and Figure 3.3b shows the difference between the retrieved surface albedo and the critical surface albedo of 0.46, a value that is estimated in the next section using the 2S-ESS model. In the calculation of the critical surface albedo, we assume that the aerosol has mineral dust properties over the desert with single scattering albedo (SSA) = 0.94 [*Kahn et al.*, 2005]. The critical surface albedo corresponding to mineral dust is much higher than the ocean albedo and is also higher than land albedos in most areas. Figure 3.3 shows that the only areas with such high albedos are deserts, where the X_{CO₂} retrieval errors are large.

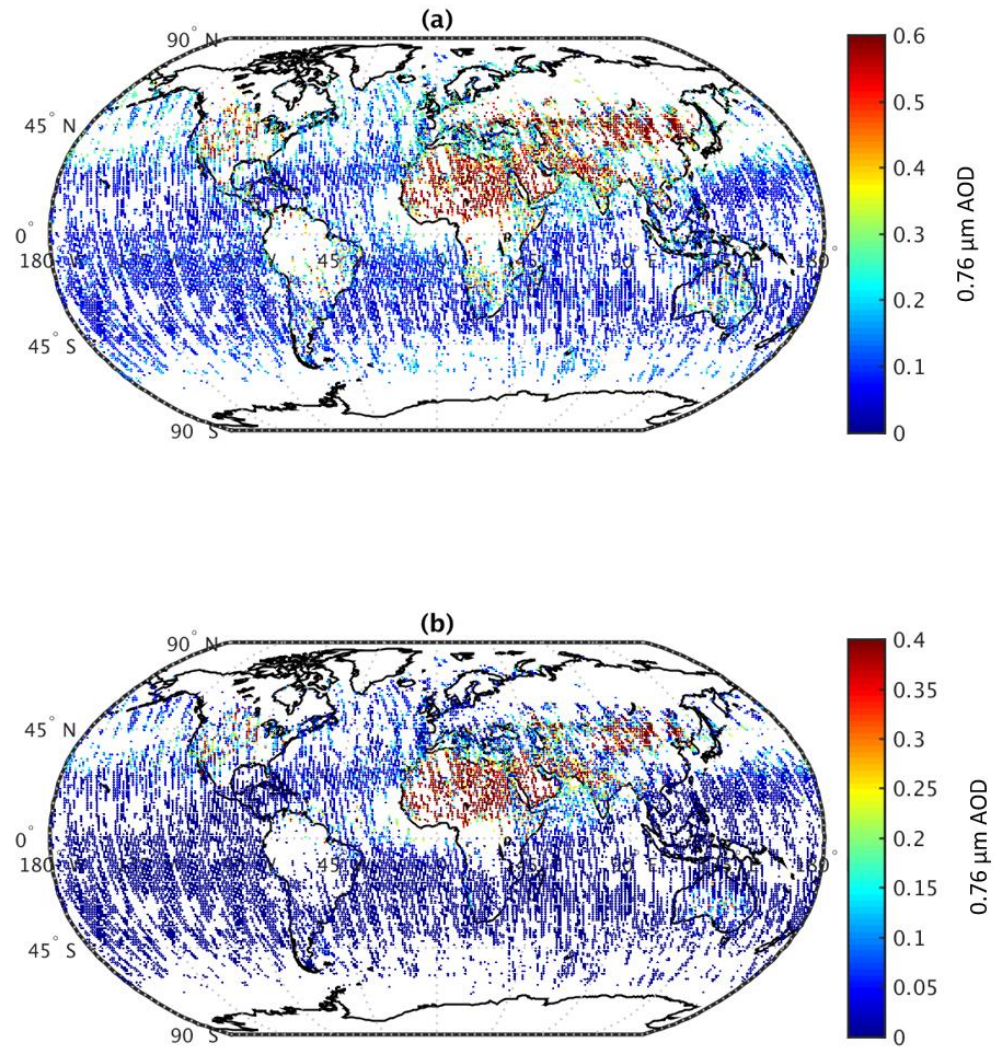


Figure 3.4 (a) Global map of the OCO-2 total AOD retrieval in April 2015. AOD values are shown in the O_2 $0.76\ \mu\text{m}$ absorption band. (b) Same as a, but for ‘type 1’ aerosol in the OCO-2 retrieval [O’Dell *et al.*, 2012], i.e. mineral dust [Kahn *et al.*, 2005].

It is well known that AOD can be large over desert regions due to wind and dust [Houweling *et al.*, 2005]. We plot the total AOD and the retrieved mineral dust AOD from the OCO-2 product in Figure 3.4. AOD values are shown in the O₂ 0.76 μm absorption band. Over the deserts, we suspect that the AOD retrieval is biased. Since mineral dust aerosol acts to change the photon path length [Houweling *et al.*, 2005], the CO₂ column abundance retrieval would also be biased, as shown in Figure 3.1. There are several reasons that lead us to attribute the X_{CO2} retrieval errors to the interaction between AOD and critical surface albedo, instead of the large AOD alone.

1. Desert is not the only region with high aerosol loadings. Over other regions with high pollution levels and large AOD, such as megacities in the eastern US and China, the X_{CO2} retrievals have much lower biases than those over desert regions.
2. Due to atmospheric circulation, dust aerosol over the Sahara Desert extends far into the Atlantic Ocean, as seen in the MODIS product [See Figure 1b in Houweling *et al.*, 2005 and Figure 8 in Remer *et al.*, 2008]. However, in Figure 3.1 and Figure 3.4, we see a clear contrast in the X_{CO2} and AOD retrievals between the ocean and the land on the boundary of the African continent. The X_{CO2} retrieval differences between the land and the adjacent ocean are most evident near the Sahara Desert. We assume that such differences in the OCO-2 product are unrealistic, although ocean retrievals are done using glint mode and land retrievals using nadir mode. We don't observe such discontinuities in other regions.

3. We examine the regions in Figure 3.1b where the X_{CO_2} retrieval fails to pass the quality check or shows a low bias, and the regions in Figure 3.3b where the surface albedo is very close to the critical surface albedo relevant to mineral dust. The two regions coincide to a large extent.

3.3. Radiative transfer modeling

The concept of critical surface albedo can be explained by a numerically efficient 2S-ESS radiative transfer model [Spurr and Natraj, 2011]. This model is better than a traditional numerical two-stream model in that the singly scattered radiation is computed exactly, while the two-stream approximation is used only for the multiply scattered radiation. It has been used in several previous studies on the remote sensing of greenhouse gases [e.g. Xi *et al.*, 2015; Zhang *et al.*, 2015]. We use a typical model atmosphere derived from the NCEP-NCAR reanalysis data [Kalnay *et al.*, 1996]. The model atmosphere includes 70 layers from the surface to the top of atmosphere. Absorption coefficients for all absorbing gases are obtained from the HITRAN database [Rothman *et al.*, 2008]. Rayleigh scattering is included in the calculation. To simulate OCO-2 nadir observations in the mid-latitude, we assume that the viewing zenith angle is zero, while the solar zenith angle is set to 45° . The incoming solar flux is assumed to be unity for all wavelengths (we effectively calculate the dimensionless reflectance). Aerosol scattering in this model is isotropic. The AOD is distributed evenly within the boundary layer below 800 hPa. The isotropic scattering assumption is equivalent to the Delta-Eddington approximation of a more realistic forward-peaked dust aerosol phase function

[Wiscombe, 1976]. This assumption has minor impact on the accuracy of radiative transfer calculation, and does not influence the conclusions in this study with respect to surface albedo and SSA. Figure 3.5a-c shows the simulated spectra in the 2.0 μm strong CO_2 band, 1.6 μm weak CO_2 band, and 0.76 μm $\text{O}_2\text{-A}$ band. Water vapor absorption is not included in this model.

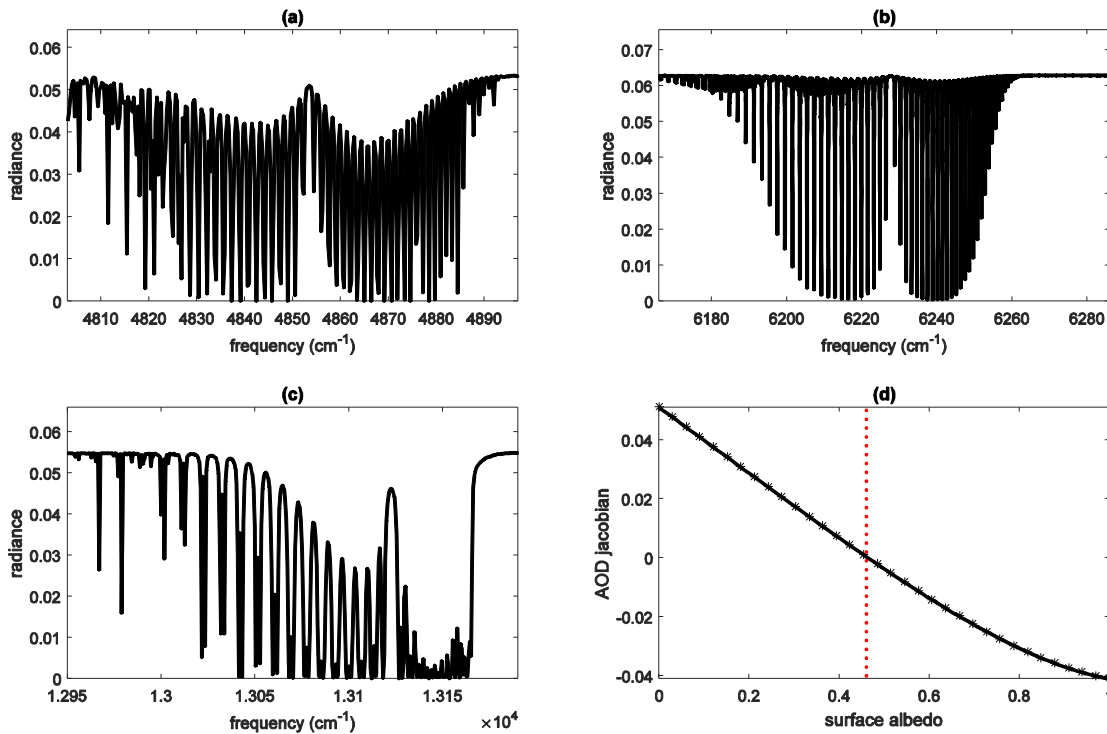


Figure 3.5 (a) Spectrum of 2.0 μm strong CO_2 band. (b) Spectrum of 1.6 μm weak CO_2 band. (c) Spectrum of 0.76 μm weak $\text{O}_2\text{-A}$ band. (d) AOD Jacobian in the continuum as a function of surface albedo. The critical surface albedo (0.46) is marked by the red dotted line.

Intuitively, increasing AOD in the atmosphere will change the continuum radiance since aerosol scattering changes the apparent albedo. We assume that the aerosol SSA is fixed for mineral dust; however, the surface albedo may vary widely

across different regions. Figure 3.5b shows the variation of the AOD Jacobian (derivative of radiance with respect to AOD) in the continuum of the 1.6 μm weak CO_2 band as a function of surface albedo. Mineral dust aerosol increases the apparent albedo over a dark surface and decreases the apparent albedo over a bright surface. Of interest, then, is the transition point at which the derivative of the radiance with respect to AOD changes sign (Equation 3.1). In Figure 3.5b, this point is marked by the dotted red line ($\alpha_c = 0.46$). Mathematically we can derive it as follows:

$$\frac{\partial R(\text{AOD}, \alpha_c)}{\partial \text{AOD}} = 0 \quad (3.1)$$

Equation 3.1 can be solved numerically using a radiative transfer model. As shown in *Seidel and Popp* [2012], α_c is primarily a function of aerosol SSA. Aerosols with larger SSA correspond to larger critical surface albedo values. In addition, the value of α_c is also associated with many other factors such as viewing geometry and aerosol height distribution.

In an optically thick atmosphere, the value of α_c can be roughly estimated as the reflectance of an infinitely thick atmosphere [*Goody and Yung*, 1989]:

$$\alpha_c = R_{\text{inf}}(\omega_0) = \frac{1 - \sqrt{1 - \omega_0}}{1 + \sqrt{1 - \omega_0}} \quad (3.2)$$

where ω_0 is the aerosol SSA. This is based on the assumption that the incoming solar flux is approximated by an isotropic diffusive flux in the atmosphere. Equation 3.2 gives a simple analytic relationship between α_c and ω_0 . The critical surface albedo is a monotonically increasing function of aerosol SSA, which is

consistent with the numerical results in *Seidel and Popp* [2012] and *Wells* [2012]. However, in an optically thin atmosphere, Equation 3.2 would overestimate the value of α_c . In this case, the critical surface albedo needs to be solved numerically using a realistic radiative transfer model.

The aerosol SSA is defined as the ratio between the scattering optical depth and the total extinction optical depth. Within the absorption line, gaseous absorption must be added on to the aerosol extinction optical depth; therefore, the relationship between SSA and critical surface albedo no longer holds. An important implication is that, if the surface albedo approaches the critical value, it is difficult to retrieve AOD. In this scenario, the sensitivity of the reflected radiance to AOD will decrease, and retrieval errors for both AOD and CO₂ will increase (Figure 3.2).

In an atmosphere with both aerosol scattering and gaseous absorption, this relationship for the critical surface albedo only holds in the continuum. Within the absorption line, the derivative of radiance with respect to AOD is not zero. In Figure 3.6, we zoom in on a single absorption line in the 1.6 μm weak CO₂ band and calculate the Jacobians with respect to AOD and CO₂ total column (scaling factor) over a low albedo surface and a surface with albedo close to α_c . Over a low albedo surface, increasing AOD has two effects: 1. increasing the radiance as the aerosol appears to be brighter than the surface; 2. changing the apparent absorption as the scattering modifies the photon path length. In Figures 3.6c and 3.6d, the AOD and CO₂ Jacobians are easy to distinguish. However, over a surface with albedo close to α_c , increasing AOD does not change the radiance in the continuum. In this scenario, the only effect of aerosol scattering is to change the apparent absorption.

Therefore, the AOD and CO₂ Jacobians, as shown in Figures 3.6a and 3.6b respectively, have almost the same shape. At low spectral resolution, the signals from AOD and CO₂ would not be distinguishable in the observations.

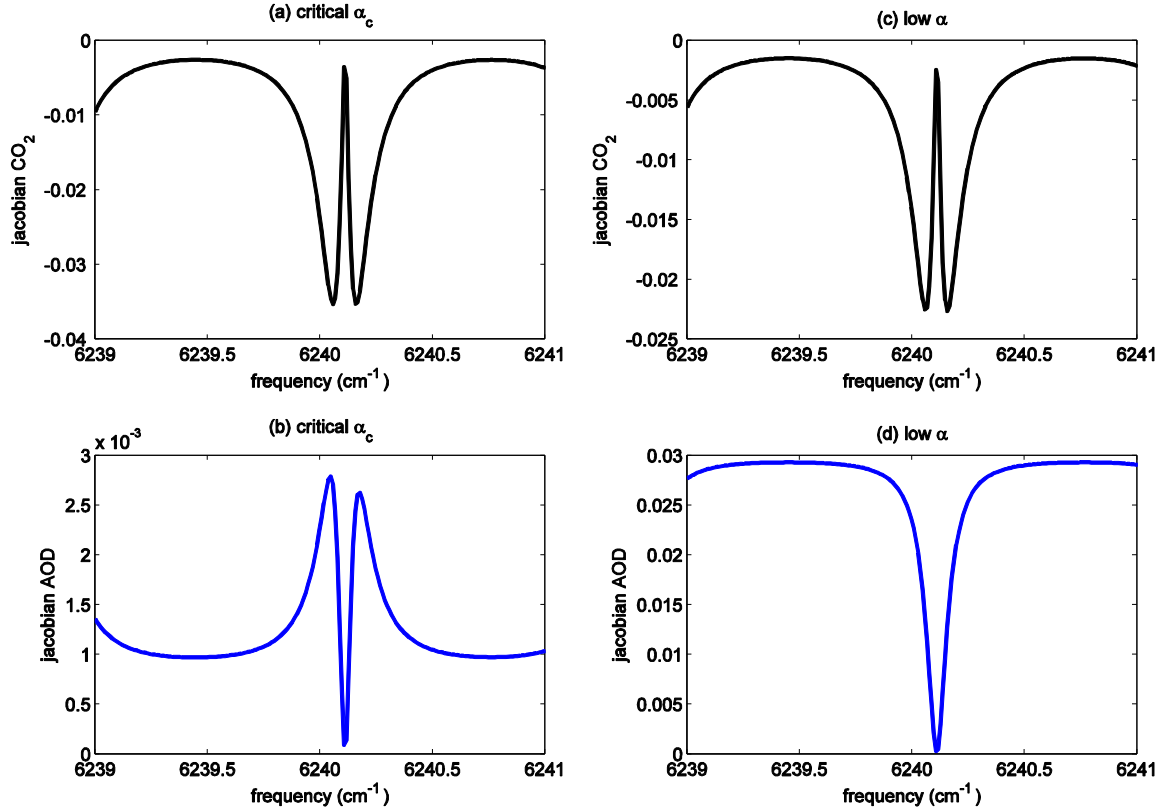


Figure 3.6 Jacobians of CO₂ and AOD in a single line, generated by the 2S-ESS model. (a) Jacobian of CO₂ total column over a surface with albedo close to α_c (0.46). (b) Jacobian of AOD over a surface with albedo close to α_c (0.46). (c) Same as (a), but over a low albedo (0.2) surface. (d) Same as (b), but over a low albedo (0.2) surface.

Using the 2S-ESS model, we can study the retrieval error caused by the surface albedo being close to the critical value. Here, retrieval error is defined as the difference between the retrieved state variables and the truth. It is different from

the posterior error, which is computed from the *a posteriori* covariance and depends only on the measurement noise. OCO-2 uses an optimal estimation approach to retrieve X_{CO_2} and other state vector variables [Rodgers, 2000] based on minimizing the following cost function:

$$\chi^2 = [\mathbf{x}_i - \mathbf{x}_a]^T \mathbf{S}_a^{-1} [\mathbf{x}_i - \mathbf{x}_a] + [\mathbf{y} - \mathbf{F}(\mathbf{x}_i)]^T \mathbf{S}_e^{-1} [\mathbf{y} - \mathbf{F}(\mathbf{x}_i)], \quad (3.3)$$

where \mathbf{x}_i is the state vector, \mathbf{x}_a is the *a priori* state vector, $\mathbf{F}(\mathbf{x})$ is the forward model, \mathbf{y} is the measurement, \mathbf{S}_a is the *a priori* covariance matrix, and \mathbf{S}_e is the measurement error covariance matrix.

We use two quantities to determine the retrieval quality and precision: degrees of freedom (d) and information content (H). They are calculated using Equations 3.4 – 3.5.

$$d = \sum_i \lambda_i^2 / (1 + \lambda_i^2), \quad (3.4)$$

$$H = \frac{1}{2} \ln(|(\mathbf{K}^T \mathbf{S}_e^{-1} \mathbf{K} + \mathbf{S}_a^{-1}) \mathbf{S}_a|), \quad (3.5)$$

where \mathbf{K} is the jacobian matrix with respect to CO_2 and AOD, and $\{\lambda_i\}$ are the singular values of the normalized jacobian $\mathbf{S}_e^{-\frac{1}{2}} \mathbf{K} \mathbf{S}_a^{\frac{1}{2}}$. Degree of freedom and information content measure, respectively, how many independent pieces of information we can obtain from the measurements, and how much the estimation of the state vector can be improved given the information from the measurement.

To simplify the problem, we set up a retrieval scheme assuming that only three state variables are included in the state vector, i.e. total column CO_2 (scaling factor), AOD, and surface pressure. In the calculation, their *a priori* uncertainties are

arbitrarily assumed to be 20%, 100%, and 0.4%, respectively. They are consistent with the retrieval algorithm shown in *O'Dell et al.* [2012]. We assume that the three state variables are not correlated. Therefore, the *a priori* covariance matrix \mathbf{S}_a is diagonal. The Jacobian matrix \mathbf{K} is calculated using finite differences, and the measurement error covariance matrix \mathbf{S}_e is defined according to the signal to noise ratio (SNR). We employ the Levenberg-Marquardt (LM) algorithm [Rodgers, 2000] to minimize the cost function. The iteration in this algorithm is:

$$\mathbf{x}_{i+1} = \mathbf{x}_i + [(1 + \gamma)\mathbf{S}_a^{-1} + \mathbf{K}_i^T \mathbf{S}_e^{-1} \mathbf{K}_i]^{-1} \{ \mathbf{K}_i^T \mathbf{S}_e^{-1} [\mathbf{y} - \mathbf{F}(\mathbf{x}_i)] - \mathbf{S}_a^{-1} [\mathbf{x}_i - \mathbf{x}_a] \} \quad (3.6)$$

where γ is the parameter determining the size of each iteration step. In the retrieval tests, we generate synthetic measurements using the 2S-ESS model within the three absorption bands, as shown in Figure 3.5a-c. For simplicity, surface albedo and AOD are the same for all the three bands. We employ a spectral resolution of 0.3 cm^{-1} in the weak and strong CO_2 absorption bands, and 0.6 cm^{-1} in the $\text{O}_2\text{-A}$ band. SNR is set to be 100. Gaussian white noise is added to the synthetic data. The SNR used in the retrieval tests is lower than the OCO-2 instrument SNR [Frankenberg *et al.*, 2015]. In addition to the radiometric noise, it includes other sources of error such as uncertainties in the HITRAN spectroscopic parameters and unresolved solar lines. We assume that the *a priori* and first guess values of X_{CO_2} , AOD, and surface pressure are 380 ppm, 0.3, and 998 hPa, respectively. These values are different from the truth, which are 400 ppm for X_{CO_2} , 0.6 for AOD, and 1000 hPa for surface pressure.

Retrieval results for different values of surface albedo are listed in Table 1. We evaluate the error in the retrieved X_{CO_2} over three scenarios: a low albedo surface ($\alpha=0.2$), a surface with albedo close to α_c ($\alpha_c=0.46$), and a high albedo surface

($\alpha=0.9$). All parameters are the same for the three cases except for the surface albedo. Over a surface with albedo close to α_c , the retrieval of the three state variables suffers from degeneracy. Further, the errors in the retrieved X_{CO_2} can be as large as 3.2 ppm over a surface with albedo close to α_c , while retrieval errors over a high or low albedo surface are about 1 ppm. The large X_{CO_2} retrieval error over a surface with albedo close to α_c is related to the inaccurate AOD retrieval, which is mainly due to the loss of degrees of freedom and information content.

Table 3.1. Retrieval tests using the 2S-ESS model

	X_{CO_2} error	AOD error	Surface pressure error	d	H
low albedo (0.2)	0.97	0.0008	-0.41	2.843	11.82
critical albedo (0.46)	3.22	-0.1018	-6.22	2.565	8.09
high albedo (0.9)	1.09	0.0009	-1.89	2.850	11.12

X_{CO_2} errors are in ppm. Surface pressure errors are in hPa. Errors are defined as the difference between the retrieved state variables and the truth (retrieved - truth).

3.4. Discussions and conclusions

We have analyzed the X_{CO_2} retrieval errors over deserts, and attributed the errors to the surface albedo being close to the critical value, α_c . It is apparent that such errors,

if not taken into account, could cause large biases in the inversion of CO₂ sources and sinks. The 2S-ESS radiative transfer model provides clear insights into the physical mechanism of aerosol scattering over a surface with albedo close to α_c . In this study, the value of α_c is determined in the 1.6 μm weak CO₂ band. Surface albedos in the strong CO₂ band and O₂-A band do not necessarily satisfy the condition of critical surface albedo. Even by using all the three measured bands, we still see a significant increase in the X_{CO2} retrieval error when the surface albedo in the weak CO₂ band is close to α_c . The transition of retrieval error from a low/high surface albedo to the critical surface albedo is a smooth function. There is a significant increase in the retrieval error, and a loss of degrees of freedom, if the surface albedo falls within $\alpha_c \pm 0.1$ (Figure 3.8). We use a 2S-ESS model in this study because it is simple and can reveal the basic physics of the impact of critical albedo on X_{CO2} retrieval. We plan to explore a more realistic model in future collaborative work with the OCO-2 retrieval team.

In addition to the interaction between aerosol scattering and critical surface albedo, there are many other sources of error in the X_{CO2} retrieval, such as cirrus clouds, uncertainties in the spectroscopic parameters, and large solar zenith angles. In Figure 3.1, we also identify large retrieval errors in high latitude regions and over South America. However, these errors are probably not related to surface albedo. Retrieval errors over these regions warrant further investigation.

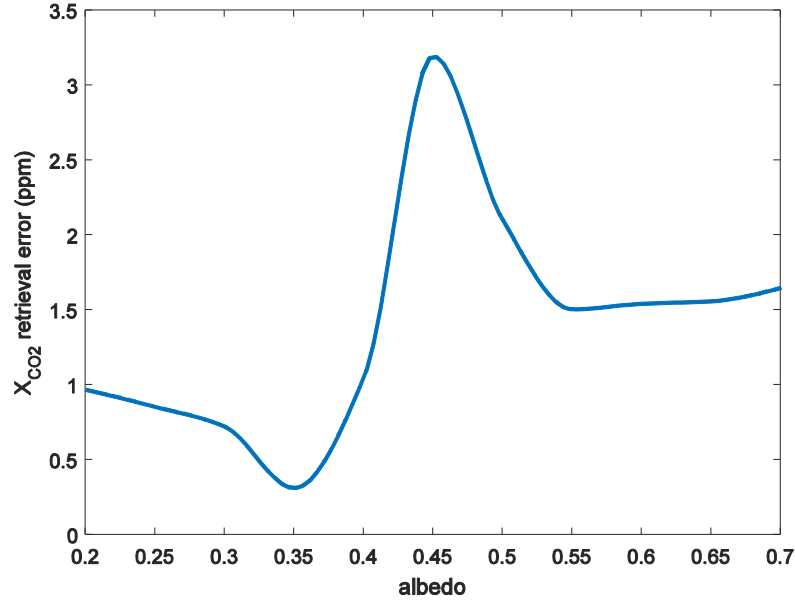


Figure 3.7 X_{CO_2} retrieval error as a function of surface albedo. The same retrieval test as shown in Table 3.1 has been done at various surface albedos.

The problem over a surface with albedo close to α_c is essentially a degeneracy in the retrieval. This idea is also tested using the analytic model we presented in Chapter 2. Although the magnitude of the AOD Jacobian is small over such a surface, its signal is almost identical to the CO_2 mixing ratio Jacobian, which leads to a loss of degrees of freedom and information content. In this scenario, the information on AOD mainly comes from the *a priori* and its retrieval has large smoothing errors. This error in the AOD retrieval will change the photon path length and influence the X_{CO_2} retrieval. We have tested synthetic data by retrieving them using the 2S-ESS model. We see a large X_{CO_2} error over a surface with albedo close to α_c , when the AOD *a priori* deviates away from the true value.

To reduce the error, we need to bring in additional information to constrain aerosol properties. If we use more accurate AOD *a priori* information and apply a stronger *a priori* constraint, X_{CO_2} retrievals over surfaces with albedo close to α_c could be improved. Given the same error in AOD estimation, the X_{CO_2} retrieval error over a surface with albedo close to α_c could be even smaller than that over a high or low albedo surface, since the jacobian of AOD over a surface with albedo close to α_c is smaller. One possible solution is to fix the surface pressure at the ECMWF [Uppala *et al.*, 2005] reanalysis value and retrieve AOD using the O_2 absorption band [Sanghavi *et al.*, 2012]. When the O_2 column abundance is known, aerosol information can be obtained from the O_2 absorption lines. Zhang *et al.* [2015] has proposed a similar solution for the retrieval of X_{CO_2} from the California Laboratory for Atmospheric Remote Sensing (CLARS) measurements. Since the ECMWF surface pressure reanalysis data is very accurate [Ponte and Dorandeu, 2003], it should be acceptable to fix the surface pressure. Retrieval tests similar to those shown in Table 1 have been done to confirm that aerosol information from the O_2 -A band could significantly reduce the X_{CO_2} retrieval error over a surface with albedo close to α_c . For OCO-2, we still need an accurate estimate of the Ångström coefficient to translate the AOD in the O_2 -A band to a value that is relevant to the weak CO_2 band. Alternatively, information on aerosols and surface albedo from other satellites, such as MISR and MODIS [Kahn *et al.*, 2005; Liang *et al.*, 2002], could also be employed to improve OCO-2 retrievals.

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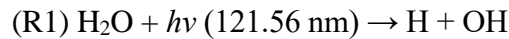
Chapter 4

RESOLVING MODEL-OBSERVATION DISCREPANCY IN THE MESOSPHERIC AND STRATOSPHERIC HO_x CHEMISTRY

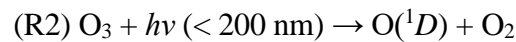
4.1. Introduction

Odd hydrogen (HO_x) species, including hydroxyl radical (OH) and hydroperoxyl (HO₂), are important catalysts of odd oxygen in the middle atmosphere [Brasseur and Solomon, 2005]. Their profiles have been observed using balloon-based measurements [Jucks *et al.*, 1998], ground-based measurements [Cageao *et al.*, 2001; Li *et al.*, 2005], and space-borne measurements [Pickett, 2006]. Other measurement techniques include ground based microwave measurements; satellite or rocket-borne absorption spectroscopy etc. Since 2004, Aura Microwave Limb Sounder (MLS) has been providing high-quality OH and HO₂ measurements in the mesosphere and stratosphere [Livesey *et al.*, 2015; Pickett *et al.*, 2008].

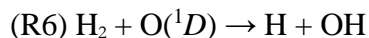
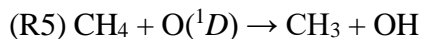
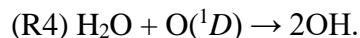
The main source of middle atmospheric HO_x is direct photolysis of H₂O by the solar Lyman- α line in the mesospheric region (>60 km):



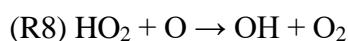
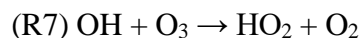
or the photolysis of O₃ and N₂O by solar UV below 200 nm and 330 nm, respectively, in the stratospheric region (<60 km) that produces O(¹D):



followed by:



OH is then converted to HO₂, and vice versa, via reactions with O, O₃ and NO:



Throughout the whole middle atmosphere, the ultimate sink of HO_x is by



[Brasseur and Solomon, 2005; Canty and Minschwaner, 2002; Wang *et al.*, 2015]. It is clear from Reactions (1 – 3) that the net source of HO_x depends sensitively to the variations of incoming solar UV solar spectral irradiance (SSI) over the rotational (~27 days) and decadal (~11 years) time scales. From satellite observations, the HO_x species have been shown to better correlate with SSI than O₃ or temperature [Rozanov *et al.*, 2006] and be good indicators of solar cycle with almost zero time lag [Shapiro *et al.*, 2012; Wang *et al.*, 2015].

Despite the simple HO_x photochemistry, a number of studies reveal discrepancies between observed and modeled HO_x concentrations. Conway *et al.* [2000] first claimed that the modeled stratospheric OH is lower than that observed by the Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI) [Summers *et al.*, 1997] while the modelled mesospheric OH is higher. They thus coined the term “HO_x dilemma” to describe this discrepancy having opposite signs in the stratosphere

and mesosphere. However, this apparent dilemma has been attributed to large uncertainties of MAHRSI data at low altitudes [Englert *et al.*, 2008]. Using standard chemistry, Canty *et al.* [2006] found that a photochemical model overestimates the HO_x concentrations in the stratosphere; while Millan *et al.* [2015] concluded that the model shows a deficit in the mesospheric HO₂. By adjusting the kinetic rates of some important photochemical reactions, Canty *et al.* [2006], Pickett *et al.* [2008] and Siskind *et al.* [2013] show that the OH concentrations observed by MLS [Pickett *et al.*, 2006] and Spatial Heterodyne Imager for Mesospheric Radicals (SHIMMER) [Englert *et al.*, 2008] are consistent with the modelled concentration.

However, since there are tens, or sometimes hundreds, of important photochemical reactions in the middle atmosphere, the choice of which kinetic rates to be adjusted to fit the observation may not be unique and subjectively dependent on our prior knowledge. For example, Canty *et al.* [2006] adjusted the reaction rates for $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$ and $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$, while Siskind *et al.* [2013] adjusted the reaction rate for $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$. To overcome the degeneracy of possible choices, here we propose an objective Bayesian optimal estimation approach that accounts for both observational and model uncertainties when selecting and adjusting model parameters. The assumptions made in this approach is that both the state variable *a priori* and the measurements follow Gaussian distribution. This approach enables us to quantify degrees of freedom (DOF) of adjusting based on the sensitivity of middle atmospheric HO_x concentrations with respect to photochemical reactions [Rodgers, 2000].

In this paper, we perform a systematic sensitivity study of mesospheric and stratospheric HO_x chemistry with respect to chemical kinetic rates and O₂ molecular cross sections. In Section 4.2, we present the Caltech-JPL photochemical model and the optimal estimation method used to adjust several model parameters. In Section 4.3, results of the optimal estimation are shown. We identify the need for reconsideration of the laboratory data and recommended rate coefficients for the H + O₂ + M → HO₂ + M reaction. Discussions and conclusions follow in Section 4.4.

4.2. Model and method

MLS is an instrument on board the Aura spacecraft, which was launched in 2004 [Waters *et al.*, 2006]. Version 3.3 MLS data are used in this study. We choose a moderately strong solar activity period in June 2005 and only use the daytime data. The lifetime of HO_x in the mesosphere depends on the concentration of several key species, such as O, O₂, and O₃; but is generally much shorter than the time scale of vertical and horizontal transport. A period at the peak of solar activity would be desirable due to the correlation between OH concentration and solar UV flux, however, it is limited by the launched date of the Aura mission. The year of 2005 is right after the maximum solar activity year. Monthly mean tropical data averaged from 25°S to 25°N are used to calculate the mean OH and HO₂ profiles (Figure 4.1). Mean solar flux data are from the Naval Research Laboratory (NRL) model [Lean, 2000]. We focus on monthly mean profiles so the results are not affected by the 27-day solar cycle variabilities.

We employ the Caltech-JPL 1-D photochemical model KINETICS to simulate OH and HO₂ profiles in the stratosphere and mesosphere [Allen and Yung, 1981]. This model contains 66 levels from the surface to 130 km altitude. Vertical transports are parameterized using eddy diffusion. Model outputs are interpolated to 1:30 pm local time in order to be compared with the MLS daytime measurements. The model has been widely used for studying photochemistry on earth and other planets [e.g. Li *et al.*, 2014; Wang *et al.*, 2013]. All the reactions in this model are listed in the supplementary material.

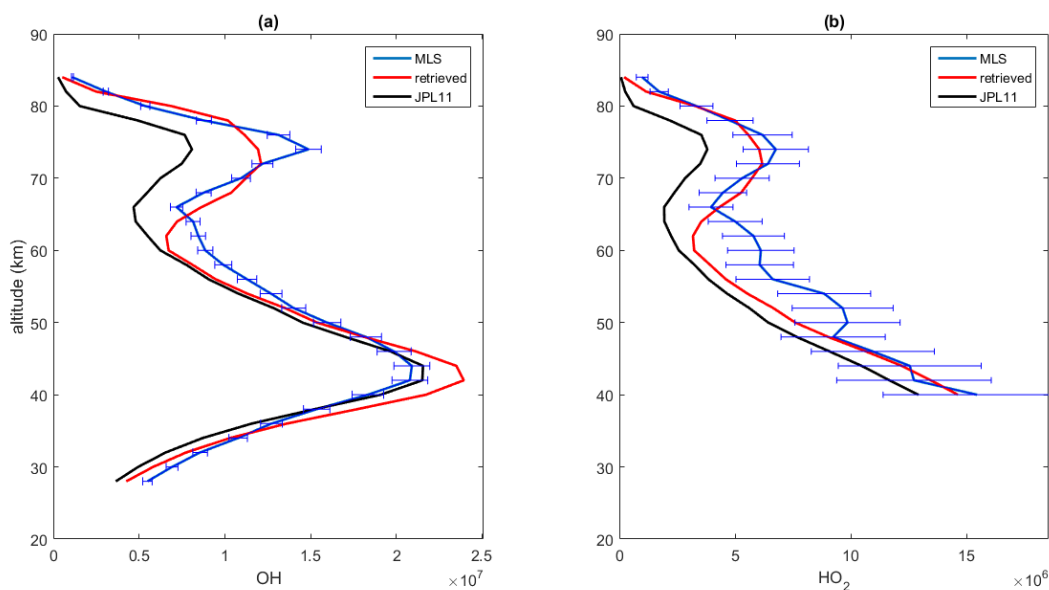


Figure 4.1. Comparison between MLS measurements (blue) and Caltech-JPL KINETICS model simulations (black and red). (a) OH concentration (cm⁻³). (b) HO₂ concentration (cm⁻³). MLS measurements are interpolated to the same pressure levels as KINETICS output and plotted as a function of altitude. Blue error bars indicate the MLS measurement uncertainties. In the comparison with the KINETICS model, MLS daytime measurements are averaged between 25°S to 25°N in latitude, and 06/01/2005 to 07/01/2005 in time. The black curve shows the model result using the

standard JPL 2011 chemistry. The red curve shows the model result using the adjusted reaction rates as shown in Table 4.1.

The goal of this study is to match the model simulation and MLS observations by adjusting a few important model parameters. Due to the simplicity of HO_x chemistry, we limit our parametric study to chemical reaction rate constants and absorption cross sections. Temperature-dependent bimolecular rate coefficients are given by:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4.1)$$

where A is the collision frequency factor, hereafter referred to as reaction rate coefficient, E is the energy barrier for the reaction, T is temperature, and R = 8.31 J K⁻¹ mol⁻¹ is the gas constant. For each reaction, initial values of A and E_a/R are taken from the JPL 2011 data evaluation [Sander *et al.*, 2011], but only the A-factors are allowed to vary. For a termolecular reaction, k is expressed in terms of high- and low-pressure limiting values and their temperature dependences. We also only consider the reaction rate constant and scale the reaction rate at all pressure levels using the same factor.

In the Bayesian optimal estimation, we minimize the cost function, as shown in Equation 2, using Levenberg-Marquardt (LM) algorithm [Rodgers, 2000]. The method has been widely used for retrieving Level 2 data from the satellite-observed radiance. It is based on Bayesian approach assuming that both the measurements and the model parameters follow Gaussian distributions.

$$\chi^2 = [\mathbf{x}_i - \mathbf{x}_a]^T \mathbf{S}_a^{-1} [\mathbf{x}_i - \mathbf{x}_a] + [\mathbf{y} - \mathbf{F}(\mathbf{x}_i)]^T \mathbf{S}_e^{-1} [\mathbf{y} - \mathbf{F}(\mathbf{x}_i)] \quad (4.2)$$

In Equation 2, \mathbf{x}_i is the statevector, \mathbf{x}_a is the *a priori* statevector, $\mathbf{F}(\mathbf{x})$ is the forward model, \mathbf{y} is the measurement of OH and HO₂ concentrations as shown by the blue lines in Figure 4.1, \mathbf{S}_a is the *a priori* covariance matrix, and \mathbf{S}_e is the measurement error covariance matrix. In this study, \mathbf{x}_a is defined as the recommended values in the JPL 2011 evaluation. We assume the measurement error to be the sum of the systematic error σ_{sys} and random error σ_{rand} as $\sqrt{\sigma_{\text{sys}}^2 + \sigma_{\text{rand}}^2}$. Random errors are calculated from the monthly OH and HO₂ data retrieval error. We set the systematic error of OH to be 5% and HO₂ to be 20%, according to the MLS product description [Livesey *et al.*, 2015]. OH and HO₂ profiles and their assumed uncertainties are shown in Figure 4.1. The cost function is evaluated in the altitude range where we have OH or HO₂ observations, i.e., 28 – 84 km for OH and 40 – 84 km for HO₂.

The cost function is expressed as the sum of two terms. The first one represents the contribution from the adjustments we made to the model parameters $\mathbf{x}_i - \mathbf{x}_a$, such as chemical kinetic rate coefficients. The second one, $\mathbf{y} - \mathbf{F}(\mathbf{x}_i)$, represents the difference in OH and HO₂ profiles between our model simulation and MLS measurements. The iteration process in this algorithm is:

$$\mathbf{x}_{i+1} = \mathbf{x}_i + [(1 + \gamma)\mathbf{S}_a^{-1} + \mathbf{K}_i^T \mathbf{S}_e^{-1} \mathbf{K}_i]^{-1} \{ \mathbf{K}_i^T \mathbf{S}_e^{-1} [\mathbf{y} - \mathbf{F}(\mathbf{x}_i)] - \mathbf{S}_a^{-1} [\mathbf{x}_i - \mathbf{x}_a] \} \quad (4.3)$$

where \mathbf{K} is the jacobian which measures the sensitivity of model output with respect to the perturbation in each parameter, and γ is a parameter determining the size of each iteration step. Jacobians of OH and HO₂ with respect to each reaction rate

constant are plotted in Figure 4.2 and Figure 4.3, respectively. There are many factors that control the sign and magnitude of the jacobians, such as the abundances of the reactants, the temperature dependence of the reaction rates, and the intensity of solar flux (for photochemical reactions). We select important reactions based on the values of their jacobians. There are two criteria here. 1. We require that the selected reactions have high sensitivities to the concentrations of OH and HO₂, therefore, their jacobians should be large in magnitude. 2. We require that the selected reactions do not suffer from the problem of degeneracy, i.e., we have enough DOF to constrain all of them.

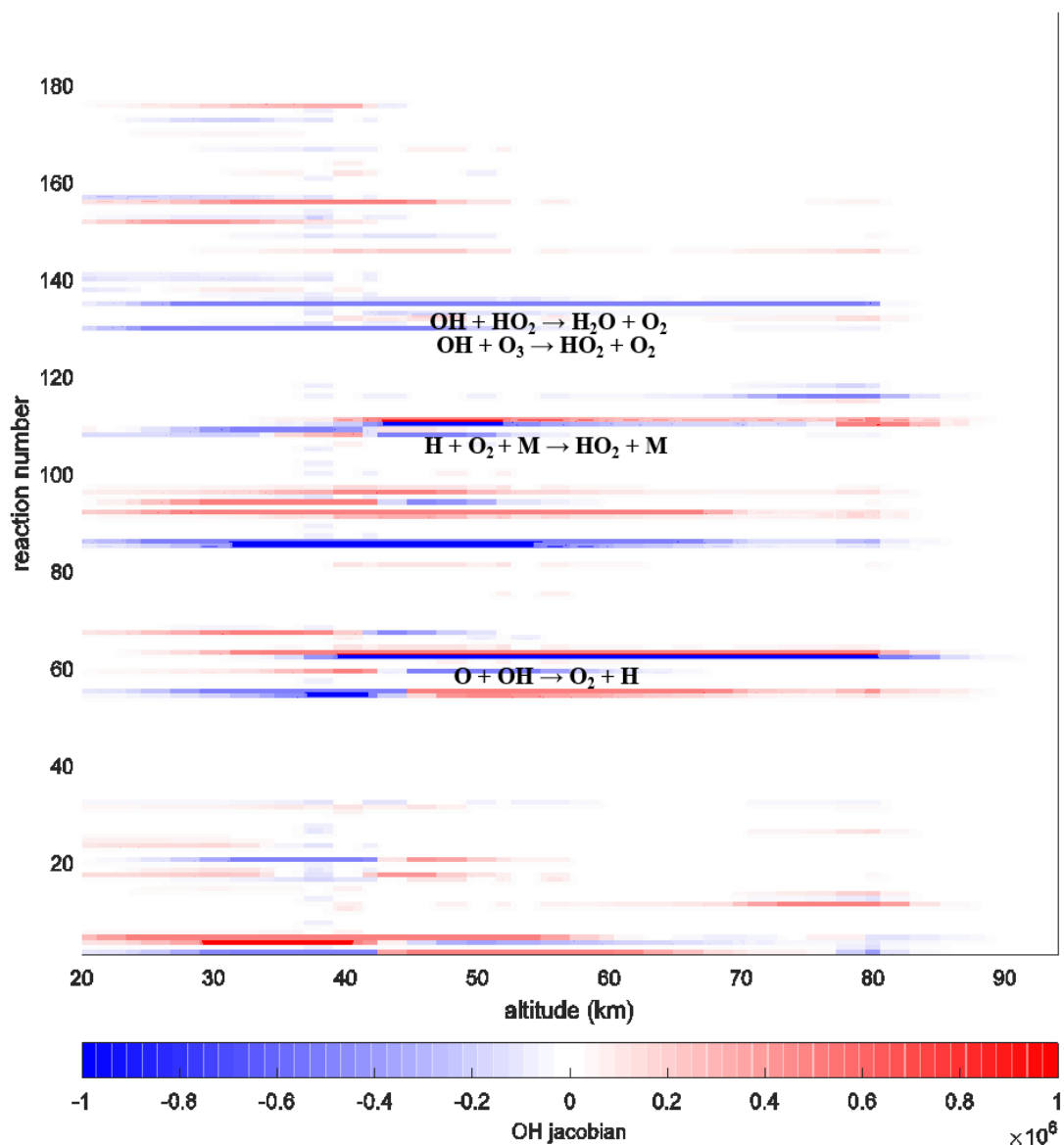


Figure 4.2. Jacobians of OH with respect to all the reaction rate constants listed in the supplementary material. Jacobian at a particular altitude is defined as the change of OH concentration (cm^{-3}) per 100% change of reaction rate constant. Important reactions are labeled in the figure. Reactions corresponding to reaction numbers are listed in the supplementary material.

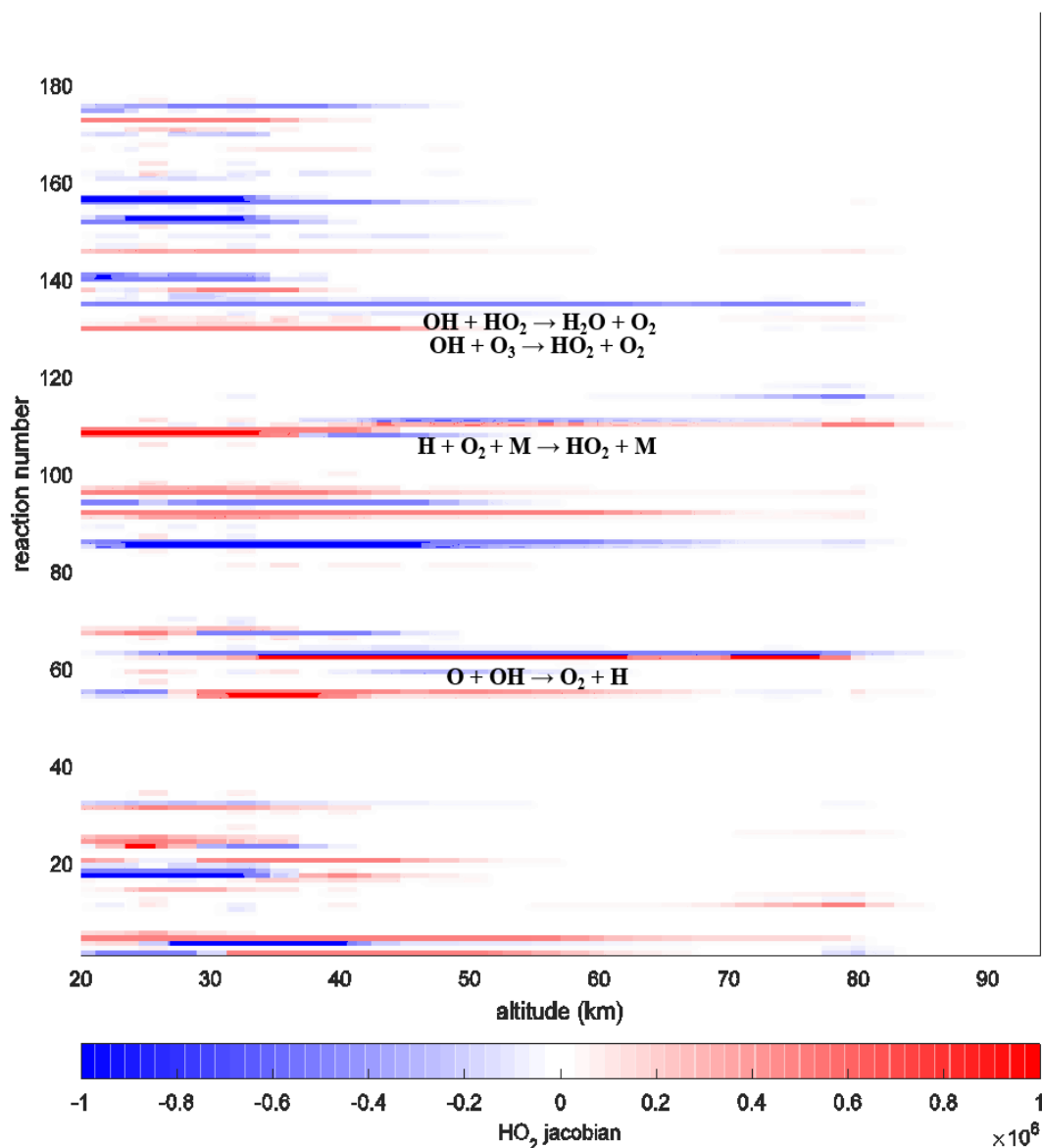
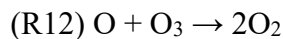
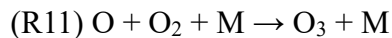


Figure 4.3. Same as Figure 4.2, jacobians of HO_2 with respect to all the reaction rate constants listed in the supplementary material. Important reactions are labeled in the figure.

A key question in the optimal estimation approach is to avoid multiple solutions. The information from the MLS measurements is not enough to constrain all the 195 reactions in this model. If too many reaction rates are adjusted, some of them may

cause degeneracy, i.e. they have very similar jacobians and therefore cannot be distinguished by the information from OH and HO₂ profiles. In this situation, we can still get a mathematically good fit of the OH and HO₂ profiles between MLS measurements and the KINETICS model simulation. However, the adjustments made to the kinetic rate coefficients are not unique, and do not have any physical meanings. For example, the following two reactions have almost symmetrically opposite effects on both OH and HO₂.

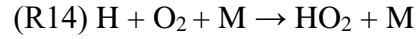


Our purpose is to exclude such similar or symmetrically opposite reactions into the optimal estimation algorithm. Otherwise they would be confounding and cause multiple solution problems. To select a list of reactions for the optimal estimation, we can calculate the DOF using 2005 June monthly mean MLS measurements (Figure 4.1), as shown in Equation 4 [Rodgers, 2000].

$$DOF = \sum_i \lambda_i^2 / (1 + \lambda_i^2) \quad (4.4)$$

where $\{\lambda_i\}$ are the singular values of the normalized Jacobian $\mathbf{S}_e^{-\frac{1}{2}} \mathbf{K} \mathbf{S}_a^{\frac{1}{2}}$. This quantity measures how many independent pieces of information we can obtain from the measurements, i.e. how many model parameters can we estimate independently from the MLS OH and HO₂ profiles. To constrain n parameters, we require a DOF larger than $n-1$. Mathematically, the DOF depends on the uncertainties of measurements and the correlations of state variable jacobians. Using all the 195 reactions, we get a DOF equal to 6.84. Apparently, it means we do not have enough information to

constrain all them. Based on the DOF analysis, we selected 4 key reactions: (R7), (R10), and the following two reactions:



These reactions are consistent with the ones suggested by *Canty et al.* [2006] and *Siskind et al.* [2013]. OH and HO₂ jacobians with respect to these reactions are plotted as a function of altitude in Figure 4.4. These 4 reactions are independent and determine the OH and HO₂ abundances at different altitudes. Their reaction rate constant uncertainties are 20%, 30%, 15%, and 15%, respectively, according to the JPL 2011 evaluations. The uncertainty values are used as diagonal components in \mathbf{S}_a

Another important model parameter that has not been considered in previous works is the O₂ absorption cross section at Lyman- α wavelength. Figure 4.5a shows the O₂ absorption cross section as a function of wavelength. An obvious feature is the particularly small value at Lyman- α [*Liang et al.*, 2007], which is very difficult to be measured accurately in the laboratory and may thus be subject to large uncertainty.

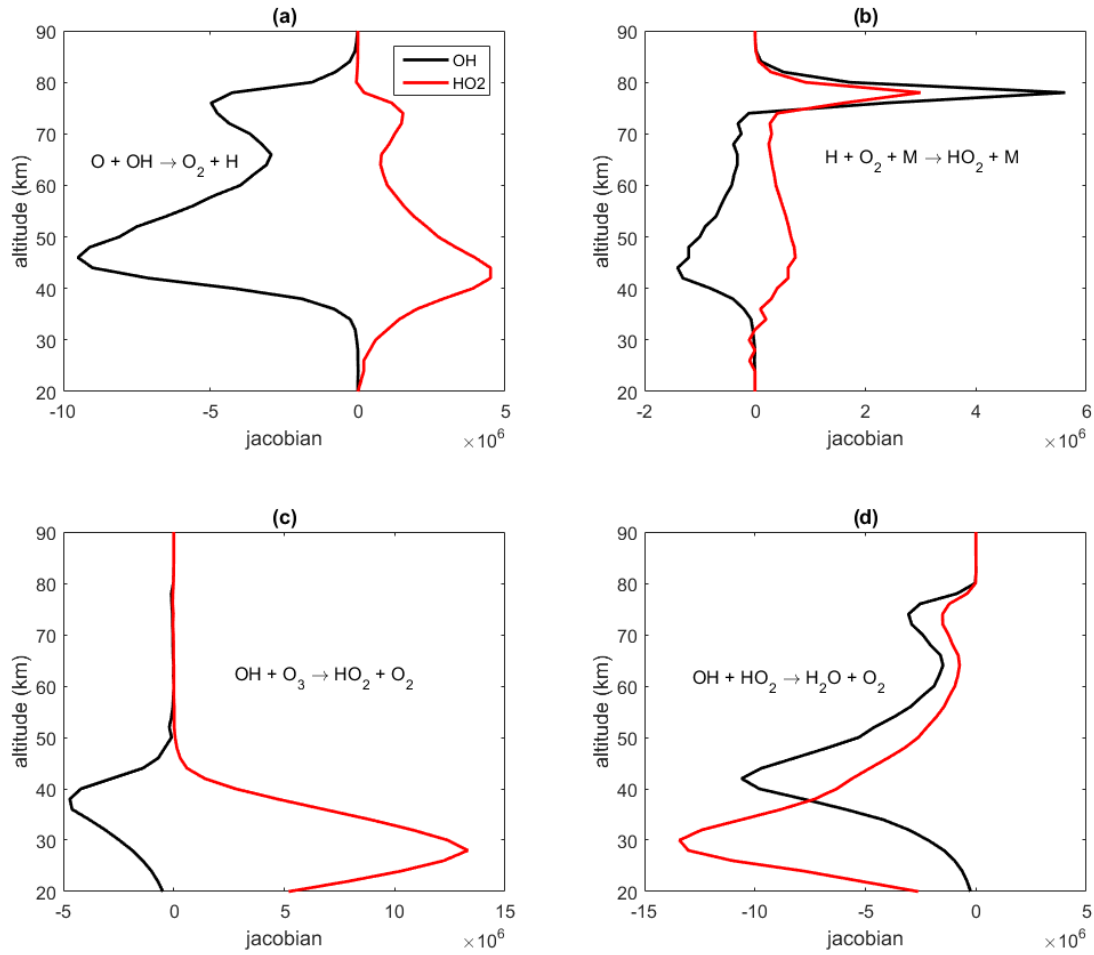


Figure 4.4. Jacobians of OH (black) and HO₂ (red) with respect to all the reaction rate constants in the optimal estimation.

The overhead sum atmospheric optical depth at Lyman- α reaches unit above 80 km due to O₂ absorption. The weaker the O₂ absorption at Lyman- α , the deeper the solar Lyman- α can penetrate into the mesosphere, and the stronger response of the H₂O photodissociation (R1) to the 11-year solar variability. Hence, the jacobians shown in Figure 4.5b reveal that adjusting the O₂ absorption cross section at Lyman-

α has a large impact on OH and HO₂ profiles. We include the O₂ cross section at Lyman- α as another state variable in our optimal estimation and give it an uncertainty of 30%. This uncertainty includes the effect of coarse spectral resolution used in the KINETKICS photochemical model. The effective cross section also decreases as atmospheric optical depth increases, since the highest absorption cross section is stronger absorbed.

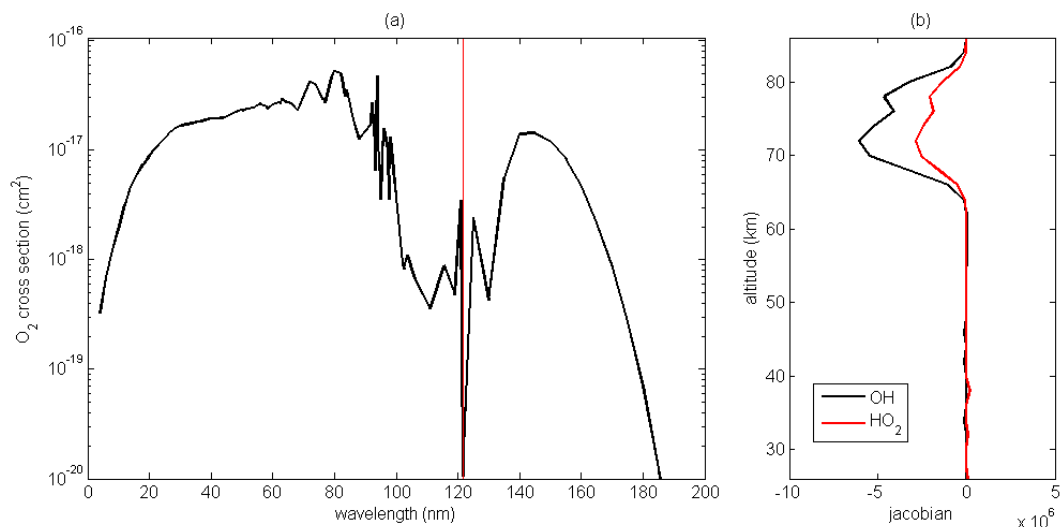


Figure 4.5. (a) O₂ cross section as a function of wavelength, Lyman- α (121.6 nm) wavelength is marked with a vertical red line. (b) Jacobian of OH (black) and HO₂ (red) with respect to the O₂ cross section at Lyman- α .

These 5 parameters have a DOF equal to 4.38. We find that including any other single reaction into the optimal estimation cannot increase the DOF by 1.0.

Table 4.1. Model parameter adjustments

reaction	uncertainty	perturbation
$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	15%	-0.3%
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	30%	+137.6%
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	15%	-9.9%
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	15%	-22.0%
O_2 cross section	30%	-60.5%

The chemical reaction rate uncertainties are the same for the total column. The same perturbations are made at each level. [Sander *et al.*, 2011]

4.3 Results

As shown in Figure 4.1, OH and HO₂ profiles generated using standard JPL 2011 chemical kinetics show a large deficit in the mesosphere. This is consistent with Millan *et al.* [2015]. We run the optimal estimation algorithm until convergence. The *posteriori* state variables listed in Table 4.1 are the adjusted model parameters which can improve the fit between model and observation. OH and HO₂ profiles generated using our adjusted model parameters are shown as the red curves in Figure 4.1. The model results after the optimal estimation exhibit much better fit to the observation. The goodness of fit is quantified by the reduced chi-square (χ_r^2):

$$\chi_r^2 = \frac{1}{N - k - 1} \sum_i \frac{(M_i - O_i)^2}{\sigma_i^2} \quad (4.5)$$

where N is the number of data points in the observation, i.e. the sum of OH profile level and HO₂ profile level, k = 5 is the number of parameters in the optimal

estimation (equal to zero for standard chemistry before we perform the optimal estimation), $M_i - O_i$ is the difference between each observation and model-simulated data point, and σ_i is the measurement uncertainty. After the optimal estimation, the value of χ_r^2 decreases from 10.01 to 2.92, showing a significant improvement in the goodness of fit. Our model is able to simulate the overall shapes of OH and HO₂ profiles. However, χ_r^2 is still larger than 1.0 in this study, probably due to the oscillatory behavior of the OH and HO₂ profiles which is a retrieval artifact [Canty *et al.*, 2006; Pickett, 2006]

In Table 4.1, the reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ requires a 137.6% increase in its reaction rate, while the measurement uncertainty recommended by JPL 2011 evaluation is only 30%. This is much larger than the perturbations made to other model parameters. There are two possible explanations. The first one is that this reaction is primarily contributing to the production of OH and HO₂ in the mesosphere (Figure 4.4b). At this altitude, pressure and temperature are extremely low. At 78 km where the jacobian of this reaction peaks, atmospheric pressure is only 0.022 hPa. Most of the measurements of this reaction are done at much higher pressure and temperature [Sander *et al.*, 2011; and references therein] and may not be accurate at such low pressure level. The characteristic times of odd hydrogen and odd oxygen increase with altitude. Reactions at high altitude may not reach steady state, but instead be in a flowing equilibrium.

Another possible explanation is the role of radiative association reaction [Vuitton *et al.*, 2012]. In the mesosphere, the pressure is low, therefore the limiting factor of

the three body reaction is the total concentration of M. At this level, the radiative association reaction ($A + B \rightarrow AB + h\nu$) may have a similar or even higher order of magnitude reaction rate than the three-body reaction ($A + B + M \rightarrow AB + M$). As a estimation, we can calculate the reaction rate of $H + O_2 + M \rightarrow HO_2 + M$ at 78 km altitude using the low pressure limit:

$$k = k_0^{300} \left(\frac{T}{300} \right)^{-n} [M] \quad (4.6)$$

In the JPL 2011 evaluation, $k_0^{300} = 4.4 \times 10^{-32} \text{ s}^{-1} \text{ cm}^6$, $n = 1.3$. T and [M] can be read from the model output as $T = 191.6\text{K}$, $[M] = 6.32 \times 10^{14} \text{ cm}^{-3}$. To compensate for the 137.6% increase in the three body reaction rate for $H + O_2 + M \rightarrow HO_2 + M$, a radiative association reaction rate for $H + O_2 \rightarrow HO_2 + h\nu$ is needed as $6.82 \times 10^{-17} \text{ s}^{-1} \text{ cm}^3$. While the radiative association reaction rates have never been measured, *Vuitton et al.* [2012] calculated several radical-molecule reaction rates theoretically using transition state theory. Our estimated reaction rate for $H + O_2 \rightarrow HO_2 + h\nu$ is consistent with their results. According to *Vuitton et al.* [2012], the contribution of the photo association reaction in a two-heavy-atom radical-radical reaction rate coefficient is in the order of $1.0 \times 10^{-17} \text{ s}^{-1} \text{ cm}^3$. As a test, this reaction is added to our 1-D KINETIC model with a nominal reaction rate of $1.0 \times 10^{-17} \text{ s}^{-1} \text{ cm}^3$. The jacobians of OH and HO₂ with respect to this new reaction exhibit the same sharp peaks in the mesosphere, as the jacobians with respect to the three body reaction $H + O_2 + M \rightarrow HO_2 + M$ (Figure 4.6). The values of its jacobians also confirm our estimation of the required radiative association reaction rate.

We have used the 2011 JPL reaction rate coefficient estimations and take into account both the stratospheric and mesospheric peaks in the OH and HO₂ profiles. Therefore, our results are slightly different from previous studies [e.g. *Canty et al*, 2006]. For example, the JPL 2011 evaluation for the reaction rate of $O + OH \rightarrow O_2 + H$ is 16% higher than that in the 2006 or 2002 version, which results in a better match between the model and observation in the stratospheric HO_x profiles. In addition to the reactions listed in Table 4.1, we also tried other combinations of reactions, including some NO_x reactions. Their fittings are all worse than the result we have shown above.

4. 4 Discussion and Conclusion

In this study, we have proposed a systematic approach to estimate model parameters, including chemical reaction rate coefficients and molecular cross sections from high-quality MLS satellite observations. The optimal estimation output can be used to quantify model parameter uncertainties and provide guidance to laboratory measurements for some key reactions. Such sensitivity studies require multiple runs to estimate the sensitivity of model output with respect to each parameter. Therefore, we employed a fast 1-D photochemical model with enough computation speed (\sim one hour for forward model run). Since HO_x chemistry in the mesosphere and stratosphere is simple and mainly controlled by several key reactions, the simplification in the transport in our model should not affect the results. In this model, all transports including vertical winds and gravity wave mixing [*Grygalashvyly et al.*, 2011] are parameterized using eddy diffusion. The most significant impact on the concentrations of HO_x species from this simplified

scheme is the transport of H₂O. As a test, we tried to perturb the eddy diffusivities at all altitudes to see their effects on OH and HO₂. The largest effect happens at the tropopause around 12 km, where H₂O is transported into the stratosphere and mesosphere. However, the jacobian of eddy diffusivity is in the order of 10⁵, much smaller than the jacobians of important reaction rate coefficients.

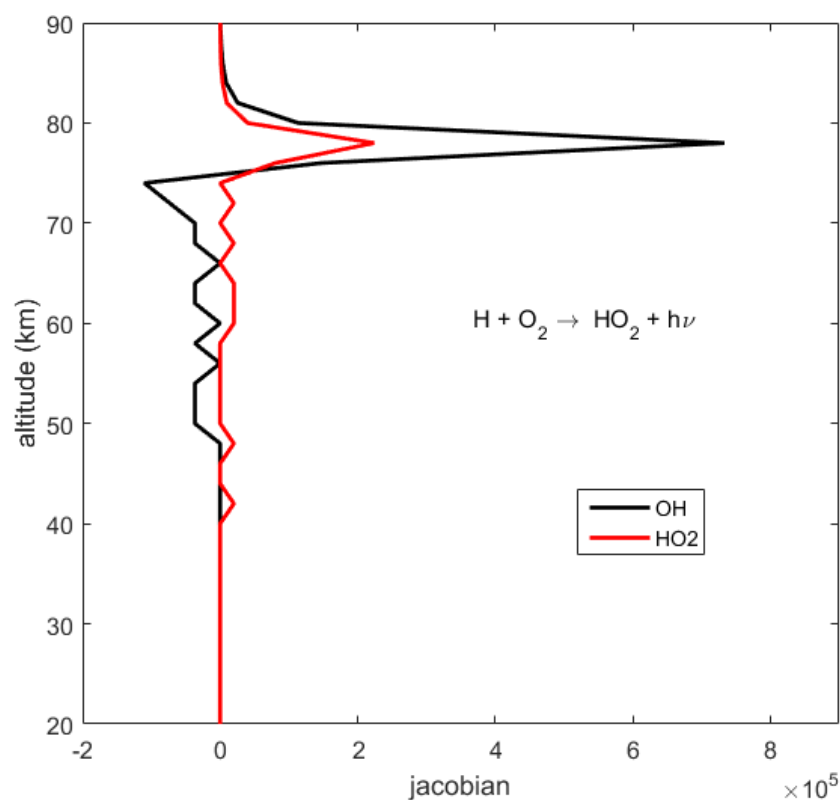


Figure 4.6. Jacobians of OH (black) and HO₂ (red) with respect to the radiative association reaction $\text{H} + \text{O}_2 \rightarrow \text{HO}_2 + h\nu$. We put this new reaction into KINETICS with a nominal reaction rate of $1.0 \times 10^{-17} \text{ s}^{-1} \text{ cm}^3$.

In previous model studies of OH, various observational constraints have been applied to reservoir species H₂O and O₃, as well as minor species such as N₂O, NO_y,

CH₄, and Cl_y [Conway *et al.*, 2000; Canty *et al.*, 2006; Picket *et al.*, 2008]. In our work, the model is time dependent, therefore we do not apply any constraints to those species. Instead, we question whether the observed OH can be simulated by an unconstrained photochemical model. As a test of our model results, we compare the model output of H₂O and O₃ profiles with MLS measurements in Figure 4.7. Our model generally agrees with observation. The impact of HO_x species on O₃ and H₂O are relatively small, since they have much larger abundances. In the mesosphere, by using the adjusted parameters in the model, higher OH and HO₂ concentrations give rise to the O₃ loss rate. Therefore, the O₃ concentration is lower than that using standard chemistry. The results are consistent with Allen *et al.* [1981] and Canty *et al.* [2006].

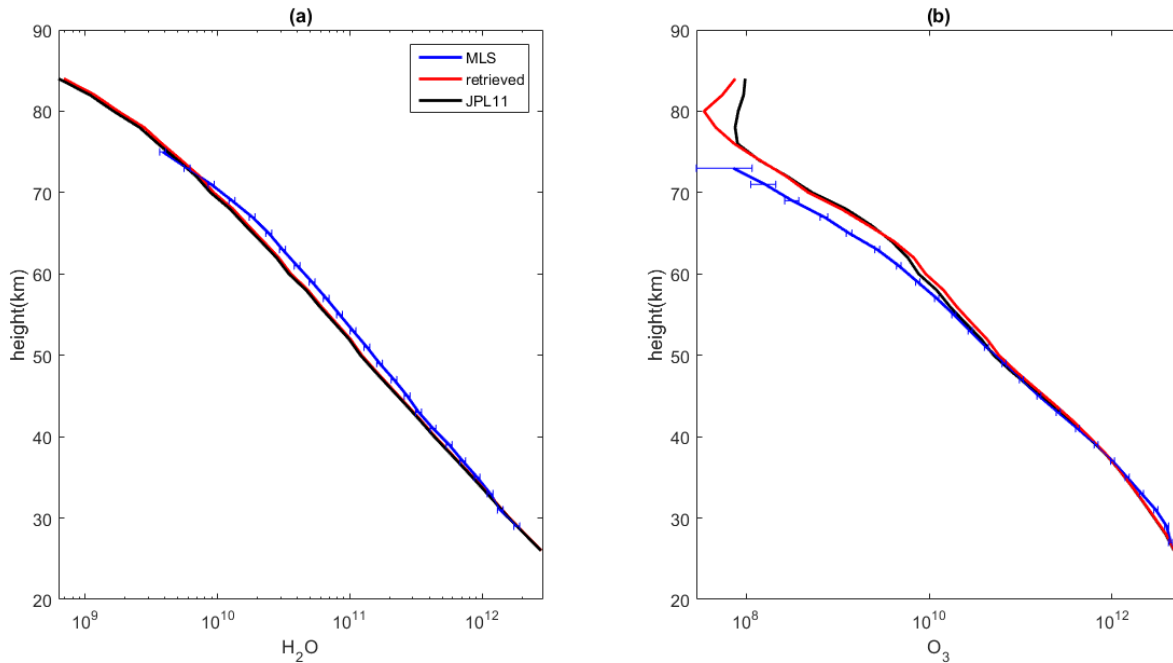


Figure 4.7. Same as Figure 4.1. Comparison between MLS measurements (blue) and Caltech-JPL KINETICS model simulations (black and red). (a) H₂O concentration (cm⁻³). (b) O₃ concentration (cm⁻³).

³). We assume the systematic error to be 5%. Concentrations are displayed in *logarithm* scale to show the differences more clearly. In a linear scale figure, the difference between model and observation is almost negligible.

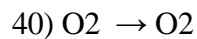
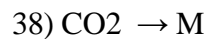
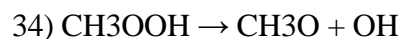
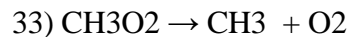
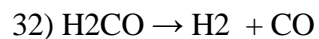
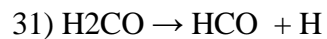
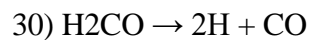
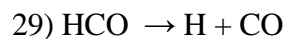
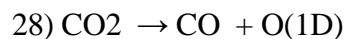
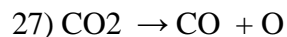
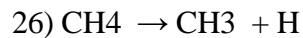
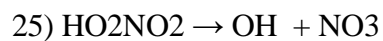
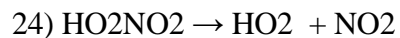
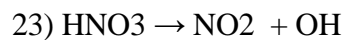
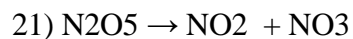
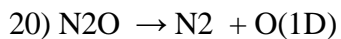
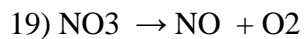
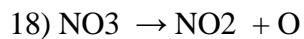
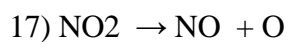
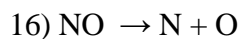
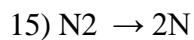
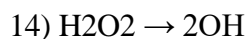
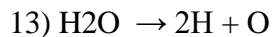
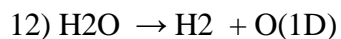
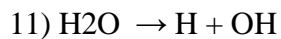
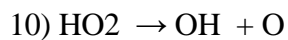
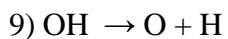
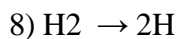
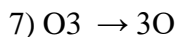
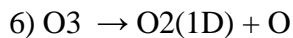
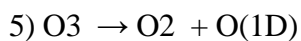
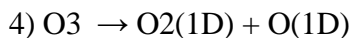
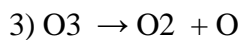
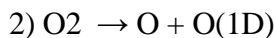
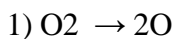
Among all the state variables listed in Table 4.1, the reaction rate of $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ and O_2 cross section require the largest adjustments. In the JPL 2011 evaluation, this reaction has the largest measurement uncertainty up to 30%, while most of the uncertainties for other reaction rates are 5% or 15%. *Siskind et al.* [2013] also shows the same result. For the O_2 cross section, in addition to the measurement error, molecular cross sections in the model could be misrepresented due to the low spectral resolution. The spectral resolution in our photochemical model varies between $20 \sim 50 \text{ \AA}$. Cross section around Lyman- α wavelength is better resolved, but still not enough to accurately represent the dramatic change up to several orders of magnitude (Figure 4.5a). To fully resolve its shape, a typical spectral resolution of less than 1 \AA is required [Ogawa, 1968]. However, this would be too expensive in terms of computational cost. The same problem also exists in a more advanced 3-D model [eg. *Garcia et al.*, 2014].

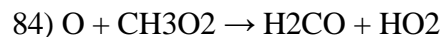
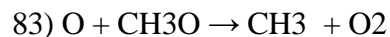
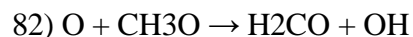
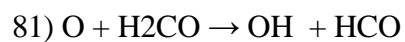
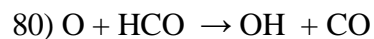
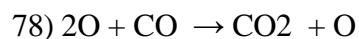
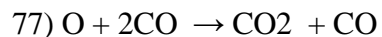
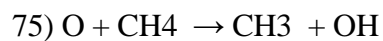
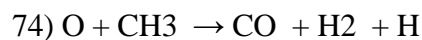
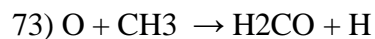
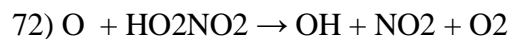
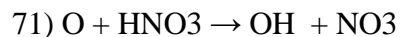
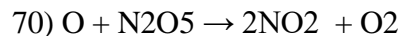
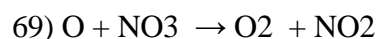
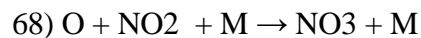
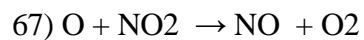
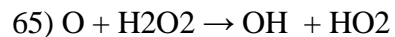
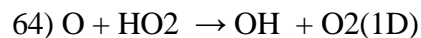
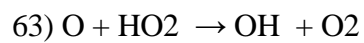
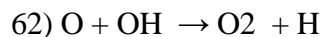
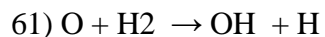
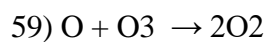
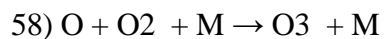
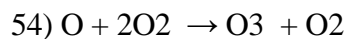
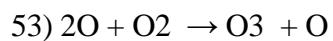
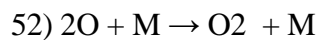
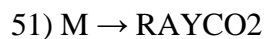
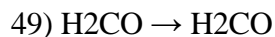
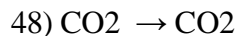
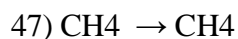
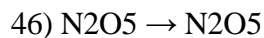
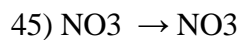
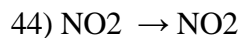
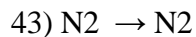
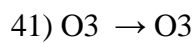
In view of the large increase in rate constant for the $\text{H} + \text{O}_2 + \text{M}$ implied by the model retrieval simulations, we have reexamined the kinetics data base for this reaction. The conclusion here is similar to that presented in *Siskind et al.* [2013]. The NASA Panel considered 11 laboratory studies of this reaction which used several different techniques over a wide range of pressures and temperatures. A large majority of these studies focused on the temperature range relevant to

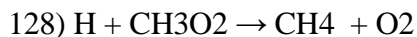
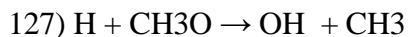
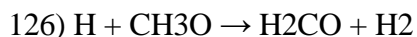
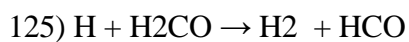
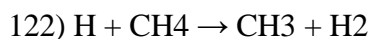
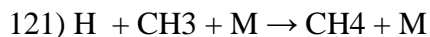
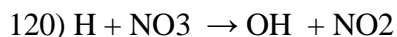
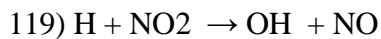
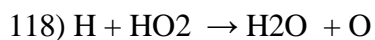
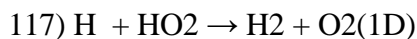
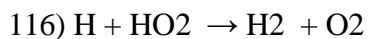
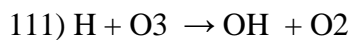
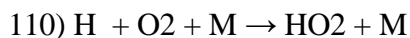
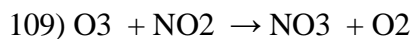
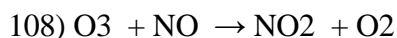
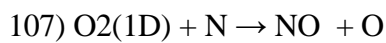
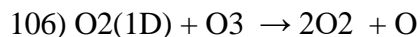
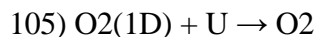
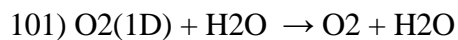
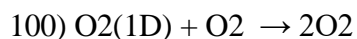
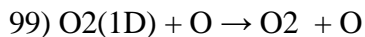
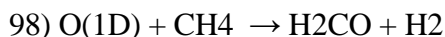
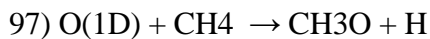
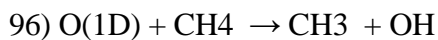
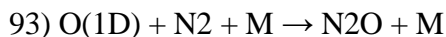
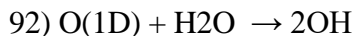
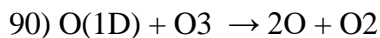
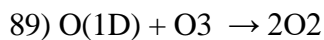
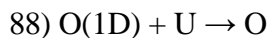
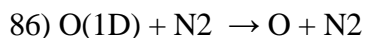
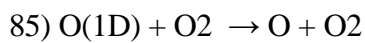
combustion conditions, $298 < T < 1500$ K. Only two studies presented data relevant to the middle atmosphere. Both *Kurylo* [1972] and *Wong and Davis* [1974] used the flash photolysis-atomic resonance fluorescence technique to measure termolecular rate coefficients below room temperature using several different bath gases. For $M = N_2$ at 220 K, *Kurylo* [1972] obtained $8.35 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ while *Wong and Davis* [1974] obtained $(8.6 \pm 1.6) \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. The rate coefficient recommended by the NASA Panel for $M = N_2$ at 220 K is considerably smaller: $6.6 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. At 298 K, where there are several additional studies, the average of the k_{298} rate coefficients is also about 25-30% larger than the NASA recommendation. It should be noted that the NASA Panel accepted the recommendation contained in a theoretical paper by *Sellevåg et al.* [2008] which was aimed at obtaining a suitable fit between two-dimensional master equation calculations and the high-temperature kinetics data base for the purposes of combustion studies. Inspection of Figure 4(b) in *Sellevåg et al.* [2008] which compares their master equation results with the lab data near room temperature for $M = N_2$ clearly shows that the theoretical results fall below all the experimental data in the termolecular pressure regime. It is clear, therefore, that the *Sellevåg et al.* [2008], and implicitly the NASA recommendation, is unsuitable for the pressure and temperature range of interest for the altitude regime considered in the present study. Although the laboratory data are very sparse in this regime, a value for the $H + O_2 + N_2$ termolecular rate coefficient that is 25 ~ 30% larger than the NASA recommendation is the best choice.

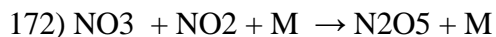
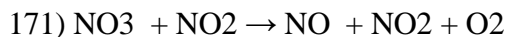
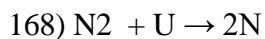
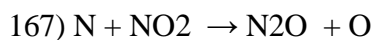
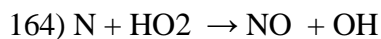
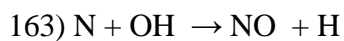
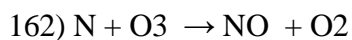
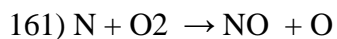
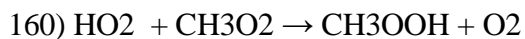
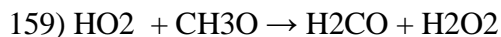
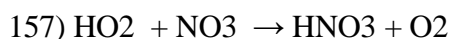
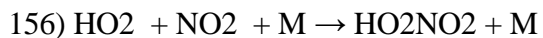
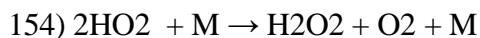
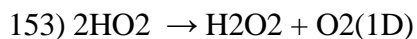
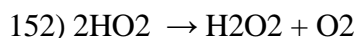
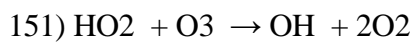
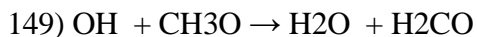
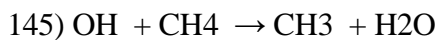
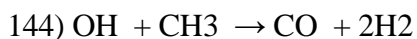
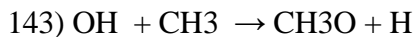
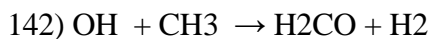
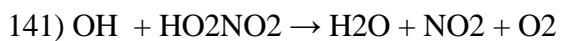
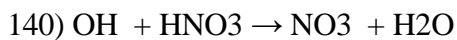
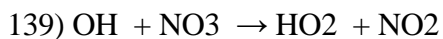
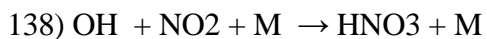
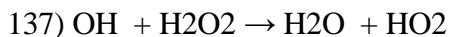
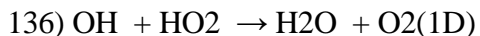
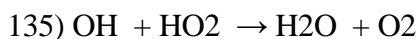
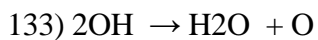
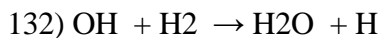
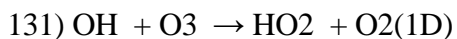
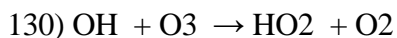
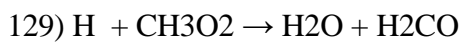
Another mechanism that might enhance the effective rate of $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$ under upper stratospheric conditions is radiative association. The reaction enthalpy, ΔH (298 K), is $-49.2 \text{ kcal mole}^{-1}$, which is much larger than the energy required to populate the low-lying \tilde{A} electronic state of HO_2 at about $17,200 \text{ cm}^{-1}$ provided that the required electronic curve-crossing is sufficiently rapid. This would also require a favorable fluorescence lifetime for the $\tilde{A} \ ^2A' \rightarrow \tilde{X} \ ^2A''$ transition, which is reasonably strong in absorption.

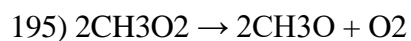
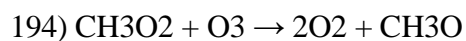
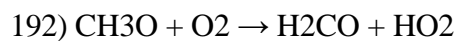
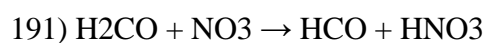
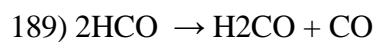
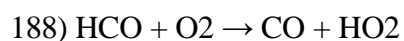
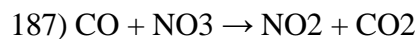
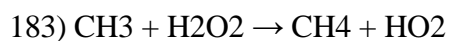
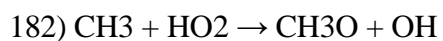
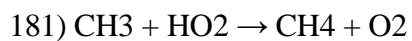
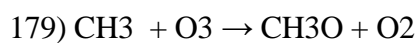
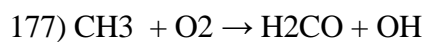
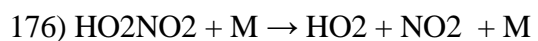
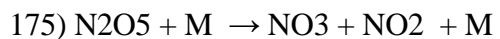
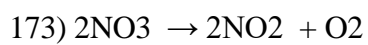
The method proposed in this study is not limited to studying HO_x chemistry. We choose to use the stratospheric and mesospheric HO_x mean profiles because they are very well measured by MLS and are mainly controlled by simple chemistry. The same method could be applied to solve other model-observation discrepancy problems. OH and HO_2 are important catalytic species for O_3 chemistry. The updated model parameters in this study can also potentially be used to model the O_3 mean profile and its responses to short- and long-term solar variabilities.

Supplementary material









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A p p e n d i x

SUBMESOSCALE TURBULENCE OVER A TOPOGRAPHIC SLOPE

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Submesoscale Turbulence over a Topographic Slope

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Abstract

Oceanic motions at submesoscales are characterized by enhanced vertical velocities, as compared to mesoscale motions, due to greater contributions from ageostrophic flows. These enhanced vertical velocities can make an important contribution to turbulent fluxes near ocean boundaries. Regions of the ocean near continental slopes are also linked to significant vertical velocities caused by advection over a sloping bottom, frictional processes and diffusion. Sloping topography may also induce large-scale potential vorticity gradients by modifying the slope of interior isopycnal surfaces. Potential vorticity gradients, in turn, may feed back on mesoscale stirring and the generation of submesoscale features.

In this study, we explore the impact of sloping topography on the characteristics of submesoscale motions. We use the MITgcm to conduct high-resolution ($1 \text{ km} \times 1 \text{ km}$) simulations of a wind-driven frontal current over an idealized continental shelf and slope. We explore changes in the magnitude, skewness and spectra of surface vorticity and vertical velocity across different configurations of the topographic slope and wind-forcing orientations. These properties are strongly modulated by the topographic slope. Additionally, submesoscale motions exhibit spatial variability across the continental shelf and slope. We find that changes in submesoscale characteristics are linked to mesoscale stirring responding to differences in the interior potential vorticity distributions, which

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are set by frictional processes at the ocean surface and over the sloping bottom. Improved parameterizations of submesoscale motions over topography may be needed to simulate the spatial variability of these features in coarser resolution models and accurately represent vertical nutrient fluxes in coastal waters.

Keywords: submesoscale, turbulence, topography, potential vorticity

1. Introduction

Dynamically, the transition between mesoscale and submesoscale motions is often marked by the loss of geostrophic balance. This is also accompanied by the generation of larger vertical velocities through ageostrophic circulations, which occurs for $Ro \sim O(1)$ (Thomas et al., 2008). Here, the Rossby number Ro is the ratio of the vertical component of relative vorticity ζ to the Coriolis frequency f . Previous studies have shown that submesoscale flows can influence vertical mixing (Klein and Lapeyre, 2009), energy transport (Klein et al., 2008), biological productivity (Mahadevan and Archer, 2000; Levy et al., 2012) and carbon export (Omand et al., 2015). However, parameterizations of submesoscale dynamics are only now being implemented in global general circulation models (GCMs) (Fox-Kemper et al., 2008), largely based on process studies in more idealized model configurations. Meanwhile, regional GCMs that directly resolve submesoscale motions show a potential increase in total eddy kinetic energy (EKE) by a factor of two (Siegel et al., 2001; Klein and Lapeyre, 2009) as compared to simulations where these motions are not resolved. The contribution of submesoscales to regional EKE may also exhibit seasonal cycles (Mensa et al., 2013; Sasaki et al., 2014).

Motions at meso- and submesoscales are intricately linked as stirring by coherent mesoscale eddies are typically responsible either for frontogenesis or filamentation that produce lateral gradients that become susceptible to submesoscale instabilities (Boccaletti et al., 2007; Capet et al., 2008). Thus variations in the spatial and temporal scales of mesoscale motions may be reflected in the intensity of submesoscale flows. Variations in the depth of the mixed layer and

the vertical stratification may also modulate the submesoscale characteristics.

Large-scale topographic slopes focus frontal currents or jets, influence the extraction of potential energy via baroclinic instability and modulate the resulting equilibrated eddy kinetic energy (EKE) of ocean flows (Hart, 1975; Poulin and Flierl, 2005; Thompson, 2010; Isachsen, 2011; Stewart and Thompson, 2015; Stern et al., 2015). Topographic constraints on ocean variability are particularly strong at the continental margins with previous studies emphasizing the impact of topographic slopes on frontogenesis and jet stability (Poulin and Flierl, 2005; Wang and Jordi, 2011; Spall, 2013). Figure 1 shows an estimate of Ro along a transect spanning the continental shelf and slope in the western Weddell Sea (Thompson and Heywood, 2008). The relative vorticity here is approximated by $\zeta = v_x$, where v and x are the cross-transect velocity and along-track distance respectively. The cross-transect velocity is calculated using the thermal wind relationship, referenced to the depth-averaged current from the glider, as documented in Thompson et al. (2014). This is a good approximation because $v_x \gg u_y$ in this region. The figure shows that Ro often exceeds values of 0.5 and frequently reaches a magnitude of $O(1)$, suggesting that balanced geostrophic motion may be insufficient to describe dynamics here and in other parts of the ocean’s continental margins.

This observational data is also consistent with recent high-resolution numerical studies with a similar shelf-slope configuration. Stewart and Thompson (2013, 2015) find that submesoscale eddies are generated over the continental shelf and shelf break, but are suppressed over the continental slope due to the strong potential vorticity gradient (Isachsen, 2011). To date, much of the work on submesoscale dynamics have been limited to idealized processes models or observational studies in strong western boundary currents (DAsaro et al., 2011; Shcherbina et al., 2013; Thomas et al., 2013) and the open ocean (Thompson et al., 2016), thus the understanding of how topographic slopes influence submesoscale dynamics is limited. An exception is a pair of studies that used a high resolution ($1/20^\circ$) numerical model to examine the generation of submesoscale dynamics in the lee of the Kerguelen Plateau in the Antarctic Circumpolar

56 Current (ACC) (Rosso et al., 2014, 2015). These simulations suggested that
57 the ACC’s interaction with the bathymetry enhanced the generation of subme-
58 soscale eddies, which subsequently played a key role in the vertical advection of
59 tracers. However, this regime is somewhat unique, since the topographic inter-
60 actions are transient as the flow moves past the plateau and the flow transitions
61 between different states, e.g. topographically-steered and open ocean. We focus
62 on a simpler configuration in this study.

63 One common characteristic of submesoscale turbulence is the generation of
64 ageostrophic motions that produce a significant asymmetry between cyclonic
65 and anticyclonic coherent vortices. Both theoretical predictions (Kloosterziel
66 et al., 2007; Lazar et al., 2013b) and laboratory experiments (Afanasyev and
67 Peltier, 1998; Lazar et al., 2013a) have shown that anticyclonic vortices are more
68 susceptible to inertial instability. This has been used to explain the preponder-
69 ance of cyclonic submesoscale eddies observed at the ocean surface (Munk et al.,
70 2000). Furthermore, Eldevik and Dysthe (2002) showed that ageostrophic baro-
71 clinic instability produces narrow frontal zones of strong cyclonic shear which
72 roll up into submesoscale cyclonic eddies. Both of these mechanisms could ex-
73 plain the results of Capet et al. (2008) and Klein et al. (2008) who demonstrated,
74 in numerical simulations of the California Current system and a baroclinically-
75 unstable zonal flow respectively, that submesoscale processes favor the gener-
76 ation of cyclonic vortices with Ro larger than one. These results also hold in
77 observations for open ocean regimes in which the fluid motion does not feel
78 any additional constraints due to changes in the water column depth (Buck-
79 ingham et al., 2016). Here we explore the robustness of these asymmetries in
80 topographically-controlled flows.

81 While this study largely focuses on the pattern of surface turbulence, it is
82 known (and shown below) that surface characteristics are linked to potential
83 vorticity (PV) distributions in the fluid interior. Modifications to PV are con-
84 centrated at the surface and sea floor due to surface wind forcing and bottom
85 friction respectively. Thomas (2005) showed that down-front wind forcing can
86 extract PV from the fluid at the surface. The low PV is then transmitted

87 through the boundary layer by the secondary circulation induced by the front
88 (Hoskins, 1982). Benthuisen and Thomas (2012) proposed that bottom friction,
89 responding to flow over a sloping bottom, could also inject or extract PV from
90 the fluid depending on the direction of the mean flow. Bottom Ekman trans-
91 port may induce changes in the isopycnal layer thickness and modulate PV in
92 the fluid interior (Thompson et al., 2014). Finally, on larger scales, we also
93 address the role of topography modifying the background PV, which changes
94 the turbulence patterns.

95 In this manuscript, we explore the hypothesis that a sloping bottom topog-
96 raphy has the potential to significantly modulate submesoscale characteristics
97 of a turbulent ocean flow. We simulate an idealized wind-forced channel, which
98 allows us to examine a range of surface wind-topography configurations. In §2
99 we present the model configuration and introduce five different experiments. In
100 §3, we present results from the numerical simulations, focusing on vorticity dis-
101 tributions, vertical velocity and energy spectra, which are common methods of
102 identifying submesoscale characteristics. We also discuss the relationship with
103 larger-scale PV distributions. Discussions of these results and our conclusions
104 follow in §4 and §5.

105 2. Model description

106 The MITgcm is employed to simulate a zonally-periodic channel on an f -
107 plane, forced by a zonally-symmetric wind stress. A schematic figure, depicting
108 the various model configurations, is shown in Figure 2. Since this study is partly
109 motivated by data collected around the continental margins of Antarctica, the
110 Coriolis parameter in the model is defined as $f = -1 \times 10^{-4} \text{ s}^{-1}$. Typically,
111 resolving submesoscale eddies requires the horizontal resolution on the order
112 of one tenth of the Rossby deformation radius (Levy et al., 2012). The model
113 domain used in this study is 640 km in the meridional direction and 320 km
114 in the zonal direction with a horizontal resolution of 1 km \times 1 km. This scale
115 is much smaller than the Rossby deformation radius, $\lambda = NH/f$, where N is

the buoyancy frequency ($\sim 4 \times 10^{-3} \text{ s}^{-1}$). These values produce a λ that varies between 10 km and 30 km, depending on the depth. In the vertical direction we have 60 layers evenly spaced from the surface to a maximum depth of $H = 600\text{m}$, giving a vertical resolution of 10 m. Density is a linear function of the potential temperature (θ) with a constant thermal expansion coefficient $\alpha = 1 \times 10^{-4} (\text{°C})^{-1}$. The initial θ (°C) profile is a function of latitude and depth,

$$\theta(y, z) = T_0 \left(1 + \frac{y}{\ell_\theta} \right) \exp \left(\frac{z}{H} \right), \quad (1)$$

where $T_0 = 19\text{°C}$ and $\ell_\theta = 80 \text{ km}$. We define $y = 0$ to be the meridional mid-point of the channel. The surface temperature at the southern and northern boundaries of the domain are 15°C and 23°C , respectively. We provide a small perturbation to the initial temperature profile to induce baroclinic instability. At the northern and southern boundaries, θ relaxes to the initial stratification within a sponge layer of 20 km width. The relaxation decays linearly to zero across the sponge layer with a maximum time scale of 3 days at the northern and southern boundaries.

At the surface, we apply a meridionally-varying Gaussian wind stress

$$\tau = \tau_0 \exp \left(-\frac{y^2}{\sigma^2} \right) \quad (2)$$

with the peak value $\tau_0 = 0.05 \text{ N m}^{-2}$ and a standard deviation of $\sigma = 40 \text{ km}$. The momentum input by the wind stress is balanced by a linear bottom friction with a constant bottom drag coefficient, $r = 1.1 \times 10^{-3} \text{ m s}^{-1}$. In this model, horizontal and vertical viscosities are set to be 1 and $10^{-5} \text{ m}^2 \text{ s}^{-1}$ respectively. Horizontal and vertical temperature diffusion coefficients are 10 and $10^{-5} \text{ m}^2 \text{ s}^{-1}$, respectively. To simulate vertical mixing in the ocean surface boundary layer, the K-profile parametrization (KPP) method (Large et al., 1997) is employed.

To study the influence of bathymetry, the simulations include a zonally-uniform topographic slope described by:

$$h(y, z) = -H \pm d \tanh \left(\frac{y}{\ell_h} \right), \quad (3)$$

where $H = 400 \text{ m}$, $d = 200 \text{ m}$ is the height of the slope relative to the maximum depth and $\ell_h = 40 \text{ km}$ is the meridional scale of the slope. The \pm sign indicates

142 that the continental shelf, the shallowest part of which is 200 m, may be either
 143 in the north (−) or the south (+). Following Poulin and Flierl (2005), we label
 144 the topographic slope as *prograde* when the shallow water is located to the
 145 left of the jet direction (recall that $f < 0$); we label the topographic slope as
 146 *retrograde* when the shallow water is to the right of the jet direction. Unlike
 147 Poulin and Flierl (2005) the jet direction is strongly forced by the surface wind
 148 stress, as opposed to responding to the propagation direction of topographic
 149 Rossby waves. The wind orientation is referenced to the initial temperature
 150 distribution. Down-front (DF) winds have the warmer water to the left of the
 151 wind stress maximum, while up-front (UF) winds have warmer water to the
 152 right of the wind stress maximum.

153 The parameter space we explore in this study is solely based on the relative
 154 orientation of the surface winds and the bathymetry. Experiments completed
 155 with different amplitudes of these properties showed qualitatively similar results.
 156 Based on alternating these two values, and including a “control” simulation with
 157 a flat bottom (DF-F), there are five different model configurations that are pre-
 158 sented in Table 1 and Figure 2. In each Experiment, the surface wind generates
 159 an along-slope current that is in the same direction as the wind stress. Thus
 160 while configurations DF-S and DF-N both have a westerly wind stress and east-
 161 ward jet, they produce retrograde and prograde jets respectively because in the
 162 former, the shallow shelf region is to the south (S experiments) while in the lat-
 163 ter the shelf is located to the north (N experiments). Similarly, configurations
 164 UF-S and UF-N produce prograde and retrograde jets respectively. Since the
 165 model simulates f -plane dynamics, the terms north and south have no dynam-
 166 ical meaning, however, the relaxation towards a colder boundary condition to
 167 the south sets the orientation of the large-scale background shear. In all of the
 168 simulations this shear is positive $\partial u / \partial z > 0$.

169 For each Experiment described in Table 1, the simulation is integrated for
 170 a period of 1000 days. The initial velocity is zero everywhere in the domain.
 171 The time required to reach a statistically-equilibrated state depends on the
 172 model configurations, however all model runs are equilibrated after 500 days.

Equilibration is determined from considering the time series of total kinetic energy (TKE) (Figure 3). Due to the suppression of linear instability growth rates over sloping topography (Isachsen, 2011), the experiments including a topographic slope take longer to reach equilibrium than the control experiment, DF-Fl. All calculations shown below represent averages over the last 200 days.

3. Results

Figure 3 provides an overview of Experiment DF-S. Available potential energy is present in all simulations due to the imposed initial temperature distribution. In experiments with down-front winds, Ekman pumping also contributes additional tilting of isopycnal surfaces. Baroclinic instability acts to relax this isopycnal tilt and generates mesoscale turbulence. Figure 3b shows a snapshot of surface θ at day 900; the sharp θ gradient just north of $y = 0$ is indicative of frontogenesis with both mesoscale and submesoscale structures apparent. While mesoscale structure is largely associated with balanced, horizontal flow, Figure 3c provides strong evidence for an active and energetic submesoscale flow by showing a snapshot of the vertical velocity w at a depth of 30 m. Near-surface w has a large magnitude (up to 10 *m/day*) and displays fine filaments associated with ageostrophic fronts. A spatial pattern in the strength of w occurs (Figure 3c) with large absolute values of w over the deeper (northern) flank of the domain, while turbulence is suppressed over the shallow (southern) flank of the domain.

The enhancement of vertical velocities is consistent with a transition towards flow with $O(1)$ Rossby number. Figure 4 shows both time-averaged and snapshots of the surface (10 m) Ro for each of the five experiments in Table 1. As in previous studies, we define local Ro as the ratio of absolute vertical vorticity and planetary vorticity:

$$Ro = \frac{\mathbf{k} \cdot \nabla \times \mathbf{u}}{f}, \quad (4)$$

where \mathbf{u} is the velocity and \mathbf{k} is the vertical unit vector. In the snapshots the surface Ro is frequently of $O(1)$. Comparing the different experiments,

201 we find the following features: (1) In all experiments, the domain is domi-
 202 nated by regions where Ro is positive. (2) Simulations that have a topographic
 203 slope tend to exhibit structure on smaller scales compared to the DF-FI Ex-
 204 periment (panel a). (3) Furthermore, in all experiments with topography, the
 205 meso/submesoscale turbulence acquires an asymmetric meridional (warm-to-
 206 cold or deep-to-shallow) spatial pattern. For example, in Figure 4(b,c), the
 207 down-front wind experiments, the warmer, “northern” flank is more energetic
 208 and exhibits larger values of Ro . This is true even though the topographic
 209 orientation is reversed between these two experiments. In contrast, in Figure
 210 4(d,e), for the up-front wind experiments, the colder, “southern” flank of the
 211 jet is more energetic and exhibits larger values of Ro . However, the meridional
 212 asymmetry is less dramatic in these up-front wind experiments. Since all other
 213 parameters are the same for these five experiments, Figure 4 indicates that the
 214 orientations of the surface wind stress and the bathymetric slope not only influ-
 215 ence the amplitude of the submesoscale turbulence, but also its spatial patterns.
 216 (4) Finally, the time-averaged Ro peaks in the core of the slope front current in
 217 both of the down-front wind experiments (panels b,c), while it is suppressed in
 218 the core of the jet in the up-front wind experiments (panels d,e). In contrast,
 219 Ro is uniform with latitude, outside of the sponge layers, in the flat bottom
 220 Experiment (panel a).

221 The meridional distribution of the turbulence can be further explored by
 222 considering the energy content at different spatial scales as shown by the power
 223 spectra of surface kinetic energy (KE) and vertical velocity (Figure 5). In each
 224 panel, the domain is partitioned into regions on the northern (black, $100 <$
 225 $y < 300$) and southern (blue, $-300 < y < -100$) flanks of the jet as well as
 226 the jet cores (red, $-100 < y < 100$). Overall, the surface KE spectra have
 227 slopes close to k^{-2} , while the vertical velocity spectra have slopes close to k^{-1} .
 228 The spectral slope is steeper in the interior deeper ocean (not shown, see Klein
 229 et al. (2008)). For Experiment DF-S, the northern (warm) flank has a larger
 230 KE spectral amplitude. The northern flank also exhibits larger amplitude in
 231 the vertical velocity spectral curve, consistent with the asymmetry in Figure

4b. In addition to having a larger amplitude, Figure 5d also shows that the northern flank surface vertical velocity spectra has a slope of $k^{-0.57}$, which is significantly shallower than in all other simulations. A shallow slope implies a greater proportion of energy is found at higher wavenumbers or smaller scales. In the control Experiment, DF-FI, surface KE and vertical velocity spectra do not show significant north to south differences in either amplitude or spectral slopes. The north-to-south asymmetry near the surface is largest in Experiment DF-S. The spectral slope in Experiment DF-N is similar to Experiment DF-S, although the amplitude is larger in DF-S. In the UF experiments, where the wind forcing is to the opposite direction of the thermal-wind balanced flow (Experiments UF-S, UF-N), the surface turbulence spectra is not modified as strongly by the bathymetry. Kinetic energy and vertical velocity spectra in Experiments UF-S and UF-N are similar to the control Experiment DF-FI (not shown).

In all experiments, cyclonic vortices are more prevalent near the surface than anticyclonic vortices, resulting in a preference for positive Ro . As mentioned in the introduction, this is consistent with many previous studies (Munk et al. (2000), Lazar et al. (2013b), Buckingham et al. (2016) to name a few), and is a possible signature of the flow’s geostrophic imbalance. In each of our simulations, we choose a shallow layer at 10 m depth and calculate the Ro probability density functions (PDF) as shown in Figure 6a. The mean PDFs for all experiments show an asymmetric distribution between positive and negative values with larger tails on the positive side. The skewness, as measured by the third moment of Ro , is positive in all experiments.

Away from the surface, Ro decays to smaller values, roughly by a factor of 3 at 180 m depth (Figure 6b, also shown in Klein et al. (2008)). PDF skewness of Ro in the interior also decreases to smaller values compared to that close to the surface, and in DF-N, the skewness of Ro decays altogether. The relative strength of the skewness across the different experiments remains unchanged away from the surface. The down-front wind experiments, DF-N and DF-S exhibit the minimum and maximum values of the skewness parameter,

263 respectively, both at the surface and in the interior. The mean of these values is
 264 approximately equal to the skewness that occurs in the flat bottom experiment.
 265 This is partially a feature of the influence of the topography on the skewness
 266 giving rise to regions within a single experiment where skewness is stronger or
 267 weaker.

268 The spatially-asymmetric pattern of the flow’s turbulent characteristics across
 269 the northern and southern flanks of the jet can be linked to the potential vor-
 270 ticity (PV) gradients in the fluid interior. The Ertel PV is defined as:

$$PV = \left(f\hat{\mathbf{k}} + \nabla \times \mathbf{u} \right) \cdot \nabla b, \quad (5)$$

271 where the buoyancy b , is a linear function of θ in our model. The interior
 272 of the model domain is largely adiabatic, therefore we expect PV anomalies
 273 to be generated primarily at interfaces, for example due to the surface wind
 274 stress or bottom friction. Figure 7 shows vertical cross sections of PV with
 275 potential temperature contours for each Experiment. Due to its large variations
 276 with depth, PV is shown in a logarithmic scale. Low PV is generated near the
 277 surface frontal regions due to wind stress, inducing lateral Ekman transport as
 278 well as strong vertical mixing. At the bottom, momentum input by the wind
 279 forcing is balanced by friction. At the same time, bottom friction drives Ekman
 280 transport to the right hand side of the zonal flow. Therefore in Experiments
 281 DF-S and UF-N, bottom Ekman transport moves dense water below light water,
 282 acting as a PV source (measured by the absolute value); while in Experiments
 283 DF-N and UF-S, bottom Ekman transport extracts PV from the fluid, acting
 284 as a PV sink. These anomalies only occur on the isopycnal layers that directly
 285 intersect with the topography. With westerly wind in Experiments DF-S and
 286 DF-N, bottom Ekman transport tilts the isopycnal layers upslope in DF-S and
 287 downslope in DF-N. As a consequence, in the shallower fluid interior (around
 288 100 m depth), interior PV gradients are generated due to the change of isopycnal
 289 layer thickness. These modifications to the background stratification lead to
 290 the preferential formation of submesoscale eddies on the flank of the jet where
 291 stratification is weak. Conversely, submesoscale eddies are suppressed over the

flank of the jet where the stratification is intensified. For the experiments where the winds are easterly (UF-S and UF-N), the interior PV tends to be larger (Figure 7), and therefore the distribution of Ro is different (Figure 4). For the UF cases, the outcropping isopycnals are advected southward, which both flattens the isopycnals generates a stronger vertical stratification on the northern flank of the jet.

In the flat bottom Experiment DF-F1, the PV structure is more uniform in the vertical direction. Critically, only a small temperature or density range outcrops on the bottom. The isopycnals that outcrop vary over relatively large scales (approximately the domain size). Thus Ekman transport is unable to generate large PV anomalies near the bottom in this experiment. By comparing Experiment DF-F1 with other experiments, we also confirm that PV changes are mainly attributed to the modulation of bottom topographic slope, and not to the surface wind forcing alone.

To show the coherent PV patterns from the bottom to the surface, in Experiment DF-S for example, we project PV onto different isopycnal layers in Figure 8. The PV on the three layers shows similar patterns, related to the anomalies either due to the wind forcing at the surface or the bottom friction. Even on the $14^\circ C$ isopycnal layer which neither intersects with the surface nor the bottom, we still see PV patterns affected by the layer thickness modulations from above and below. This shows that PV sources/sinks at the bottom due to Ekman transport can affect the stratification in the isopycnal layers above. Corresponding time and zonal mean PV fluxes are also calculated in each isopycnal layer as $\overline{\langle PV \cdot \mathbf{v} \rangle}^{x,t}$, where \mathbf{v} is the interpolated meridional velocity in each snapshot. Mean PV flux has opposite sign to the PV gradient. In the layer that intersects with the slope, negative PV flux is generated near the slope and results in a low PV region.

319 4. Discussion

320 4.1. Spectral slope

321 The spectral representation of the velocity field has been a powerful tool
322 for distinguishing flows in mesoscale and submesoscale regimes. At the outset
323 of the study, we described the submesoscale range as those scales at which
324 Ro becomes $O(1)$ and therefore, ageostrophic motions, by definition, become
325 relevant. Callies and Ferrari (2013), using an objective rather than a dynamic
326 definition, identified submesoscales using a wavelength range from 1 to 200 km,
327 and used observation-based spectra of eddy kinetic energy to determine the
328 contribution from balanced and unbalanced motions at these scales. In the Gulf
329 Stream region, within the mixed layer, a transition between balanced, interior
330 quasi-geostrophic motion and unbalanced, predominantly internal wave motion,
331 occurs at roughly 20 km. At scales smaller than 20 km, unbalanced motion was
332 found to dominate the energy spectrum, and spectral slopes consistent with
333 surface quasi-geostrophic (SQG) predictions (Klein et al., 2008) were not found.
334 Additionally, in a more quiescent region in the eastern Pacific, kinetic energy
335 distributions were not consistent with SQG, nor did they reveal a geostrophic
336 turbulence regime (spectral slope of k^{-3}).

337 Klein et al. (2008) concluded that near surface kinetic energy spectra show a
338 k^{-2} slope, which is significantly shallower than that in the deeper ocean (k^{-4}).
339 Mixed layer baroclinic and symmetric instabilities may enhance submesoscale
340 turbulence and flatten the spectra (Capet et al., 2008). In our simulations, sur-
341 face kinetic energy spectra show a similar slope of k^{-2} despite the introduction
342 of a continental slope. Callies and Ferrari (2013) argued that the disagreement
343 with SQG theory arose from the injection of energy in the submesoscale range
344 by small-scale baroclinic instabilities or from a coupling between surface and
345 interior dynamics. While we do not resolve internal waves in these experiments,
346 we speculate that the introduction of a topographic slope may impact the wave-
347 length at which the transition between balanced and unbalanced motions occur.
348 Both of these processes are likely to be active in producing the spectra diagnosed

349 from our simulations.

350 Callies and Ferrari (2013) found a similar near-surface k^{-2} slope when an-
351 alyzing observations from the subtropic North Pacific gyre, however they dis-
352 carded the link of this slope to SQG dynamics due to the fact that this region
353 has non-uniform stratification, from which the k^{-2} scaling arises in Klein et al.
354 (2008). For our simulations, we introduce a stratification with a vertical tem-
355 perature decay, which should result in a kinetic energy slope that is flatter than
356 k^{-2} . Finally, the spectra show a weak dependence with depth, which also con-
357 tradicts SQG theory. Thus we conclude that our shallow spectra are not results
358 of near-surface SQG dynamics, but rather with the generation of unbalanced,
359 ageostrophic motions.

360 Typical explanations for the failure of geostrophic balanced motion include
361 frontal circulations, Ekman flows, mixed layer turbulence, near-inertial oscil-
362 lations, and internal tides. We can eliminate internal tides because they are
363 not included in our simulations. However, both frontal circulations and Ekman
364 flows are likely to play a critical part in generating the flatter spectra and also
365 in explaining the diversity of spectral slopes seen across the different simula-
366 tions. To assess the importance of Ekman flows and mixed layer turbulence,
367 we have analyzed the vertical structure of the EKE in our various simulations
368 (Figure 9). Experiment DF-N shows the largest degree of vertical decay of the
369 EKE amplitude, where all the other experiments show similar levels of EKE
370 throughout the upper 200 m of the domain. The DF-N experiment also shows
371 the smallest vorticity skewness (Figure 6), which decays completely in only 180
372 m depth. This is also consistent with the fact that in Experiment DF-N the PV
373 is approximately constant throughout the water column (Figure 7).

374 Rosso et al. (2015) studied the spatial inhomogeneity in submesoscale tur-
375 bulence and proposed that topography influences submesoscale dynamics indi-
376 rectly through the interaction with the large scale flow. Here we showed that
377 kinetic energy spectra display a north to south asymmetry over the topographic
378 slope. Next we will demonstrate that this is due to the topographic modifica-
379 tion of background PV, which suppresses turbulence over one side of the domain

380 (section 4.2).

381 Compared to kinetic energy, vertical velocity is of greater biogeochemical
382 interest as it influences the transport of nutrients from greater depths to the
383 surface. In this study, we also calculate the spectra of surface vertical velocity.
384 It has a spectral slope of k^{-1} , consistent with Levy et al. (2012), in which the
385 co-spectra of $w \cdot NO_3$ are studied. Vertical velocity spectra are also strongly
386 modified by the bathymetry in both absolute value and power spectrum slope.
387 Regions with larger EKE are associated with larger vertical velocities.

388 4.2. Interior PV gradients

389 In this section, we link changes in submesoscale characteristics to the dis-
390 tribution of PV in each of the simulations. These distributions have a strong
391 impact on the characteristics and amplitude of the mesoscale vorticity field,
392 which is responsible for generating horizontal buoyancy gradients that catalyze
393 submesoscale instabilities. This relationship emphasizes the strong connection
394 between the surface submesoscale field and the interior dynamics.

395 There are three physical processes that are responsible for setting the inte-
396 rior stratification: (a) thermal forcing from the lateral boundaries; (b) modifi-
397 cation of the isopycnals over the continental slope related to PV conservation
398 (this tends to generate isopycnals that slope in a similar sense to the bottom
399 topography) (Isachsen, 2011; Stewart and Thompson, 2013) and (c) Ekman con-
400 vergence and divergence caused by frictional processes at both top and bottom
401 boundaries (Thomas, 2005). Figure 7 shows that in all simulations, a broad
402 region at the surface, which spans the latitudes that feel a surface wind forcing
403 exhibits low PV reflecting a weak surface stratification. The generation of this
404 low PV layer is due to the inclusion of the KPP parameterization scheme in the
405 numerical model, which keeps the mixed layer approximately constant at 40 m.
406 The presence of this relatively well-mixed surface layer preconditions the verti-
407 cal stratification to be weak and that can potentially generate low Richardson
408 number flows. We note that low or even positive PV values may be generated
409 in these simulations when lateral buoyancy gradients exceed the size of vertical

410 buoyancy gradients. These conditions may be suitable to mixed layer instabil-
 411 ity (Boccaletti et al., 2007; Mahadevan et al., 2010) or symmetric instability
 412 (Hoskins, 1974), which would work to restratify the mixed layer. However, for
 413 symmetric instability, our simulations do not have sufficient resolution to cap-
 414 ture the evolution of secondary instabilities that would lead to diabatic mixing
 415 (Taylor and Ferrari, 2009; Bachman and Taylor, 2014).

416 In each simulation, the wind stress generates a mean flow that is in the same
 417 direction as the surface wind stress (see contours in Figure 9). In experiments
 418 where the wind stress is *down-front*, in the sense of the thermal forcing from the
 419 boundaries, the mean wind-driven overturning increases the isopycnal tilt (Fig-
 420 ure 7). The generation of mesoscale eddies via baroclinic instability saturates
 421 this process. In the experiments where the wind forcing is *up-front*, the (Exper-
 422 iment UF-S and UF-N) the surface wind forcing is sufficiently large to generate
 423 a V-shaped pattern in the isopycnals, which will act to localize the instabil-
 424 ity processes. These surface forcings have a significant impact on the interior
 425 PV distributions. In regions where the Ekman flow is predominantly divergent,
 426 isopycnal surfaces are pushed up towards the surface, which enhances the verti-
 427 cal stratification and the background PV. This is apparent on the jet’s southern
 428 flank in Experiments DF-S and DF-N and on the northern flank in Experiments
 429 UF-S and UF-N. Conversely, the stratification and the PV is suppressed on the
 430 opposite flank. In these low PV regions, the potential for generation of sub-
 431 mesoscale processes is enhanced. This explains why in both Experiments DF-S
 432 and DF-N, turbulence is more energetic at smaller scales on the northern flank
 433 of the jet. Here the amplitude of PV is reduced as a result of convergent Ekman
 434 transport.

435 This localization of regions that are preferentially susceptible to subme-
 436 soscale motions is also apparent when comparing Experiments DF-S and UF-S.
 437 In the former, PV is minimized at the core of the jet, whereas in the latter
 438 PV is maximized at the core of the jet. Again, the Ekman transport cause the
 439 outcropping isopycnals to be advected southward, increasing the near-surface
 440 vertical stratification across the core of the jet. As a result, in Experiment DF-

441 S, the Rossby number is elevated in the jet core, while in Experiment UF-S, the
 442 Rossby number is suppressed at the jet core.

443 Fine spatial variability in the PV distributions also occurs near the bottom
 444 boundary. Figure 10 compares vertical kinetic energy as $\rho w^2/2$ in all the simu-
 445 lations, where w is vertical velocity and ρ is density. Here, frictional processes in
 446 the bottom boundary layer can, with a laterally-sheared mean flow, give rise to
 447 significant vertical velocities that influence the near-bottom stratification (Ben-
 448 thuyssen and Thomas, 2013; Ruan and Thompson, 2016).

449 Over the continental slope, Ekman overturning acts as a PV sink in Exper-
 450 iment DF-N and UF-S, resulting in a low PV region. This region is associated
 451 with large vertical velocity and Ro . We compare the vertical structures of Ro
 452 for Experiment DF-S and UF-S in Figure 11. It is evident that in Experiment
 453 UF-S, Ekman overturning due to friction produces large Ro at 300 m depth. Ro
 454 close to the bathymetry is even larger than that at 150 m depth. In contrast,
 455 for Experiment DF-S, bottom friction is a source of PV, which inhibits the gen-
 456 eration of large w or Ro . In Figure 11 a-c, Ro decays in magnitude through the
 457 water column; there is no near-bottom enhancement.

458 In summary, the interaction of surface wind forcing, a strong mean flow
 459 and a topographic slope can lead to substantial changes in the interior PV
 460 over relatively short distances. These are reflected in the characteristics of the
 461 submesoscale motions, which are more active in low PV regions.

462 *4.3. Interaction between mesoscale and submesoscale*

463 Topography influences submesoscale motions primarily through mesoscale
 464 eddies. The interaction between the mesoscale and submesoscale motions can
 465 be studied through the correlation between submesoscale vertical velocities and
 466 mesoscale EKE (Rosso et al., 2015). Isachsen (2011) has shown that eddy diffu-
 467 sivities in the ocean is sensitive to the ratio of topographic slope and isopycnal
 468 slope. In this study, all simulations with a topographic slope exhibit stronger
 469 isopycnal tilt than the flat-bottom control experiment, DF-F1. However, the
 470 equilibrated EKE levels are spatially more complex, which is due to a tendency

471 for a continental slope to dampen EKE levels. Over a steep continental slope,
 472 baroclinic instability is inhibited and EKE becomes smaller compared with a
 473 flat bottom experiment (Figure 9).

474 Comparing Figure 10 with Figure 9, we find that regions with enhanced
 475 submesoscale vertical velocities are also associated with larger mesoscale eddy
 476 kinetic energies. Similar to Ro and the vertical velocities, EKE also shows
 477 an asymmetric distribution between the northern and southern flanks of the
 478 front, with larger values associated with weaker stratification. The only counter-
 479 intuitive case is Experiment DF-N, in which submesoscale motions are enhanced
 480 in the northern flank of the front but EKE is suppressed in the same region. The
 481 low EKE in the northern flank is mainly due to the isopycnal layers that interact
 482 with both the surface and the bathymetry (Figure 6). The transport of EKE
 483 from the frontal region to the northern flank is constrained by the isopycnal
 484 layers that outcrop on the continental slope and do not extend to the northern
 485 boundary. This results in a low EKE region coupled with a weak background
 486 PV and vertical stratification that still supports a shallow submesoscale field.

487 5. Conclusion

488 In this study, we examine the modulation of surface turbulence characteris-
 489 tics related to wind-induced frontal currents formed over a topographic slope.
 490 We link the surface properties to changes in interior PV distributions related
 491 to the orientation of the surface wind stress and the continental slope. Ekman
 492 transport over a topographic slope can generate low or high PV regions in the
 493 ocean interior, associated with weak or strong stratification near the surface,
 494 respectively. We find that this variability in the surface stratification generates
 495 meridional asymmetry in the kinetic energy spectra as well as the amplitude
 496 and skewness of the Rossby number. Variations in surface submesoscale turbu-
 497 lence by the topography is mainly through the modulation of mesoscale stirring,
 498 which is evident from the correlation between near-surface EKE and the ampli-
 499 tude of turbulent vertical velocities. In addition to the modulation of surface

500 turbulence, down-slope Ekman transport also generates a low PV region near
501 the ocean floor and give rises to large vertical velocities near the ocean bottom.

502 The main conclusions of the study are summarized as follows:

- 503 1. Surface vorticity characteristics are modified by the presence of a sloping
504 bottom. Most of the persistent eddies near the surface are cyclonic.
- 505 2. The sloping bottom modifies the spectra of near-surface vertical velocities
506 and kinetic energies. Velocity spectra exhibit spatial asymmetries between
507 the northern and southern flanks of the domain.
- 508 3. Surface turbulence characteristics are linked to modifications of the inte-
509 rior PV gradients, which are generated by the Ekman transport along the
510 sea surface and along the bottom.
- 511 4. These results are not consistent with SQG theory and suggest the criti-
512 cal role of ageostrophic velocities generated both at surface and bottom
513 boundaries.

514 These results suggest that along-slope wind stress and slope orientation exert
515 substantial influence over the transport and mixing across the continental shelf,
516 with implications for the exchanges of mass, heat, salt, and biogeochemical
517 tracers in coastal waters.

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Table 1: Simulation configurations. The five experiments correspond to the schematics in Figure 2. The identifying characteristics include the wind and topography orientation. The front velocity is determined from the location where $|\bar{u}(y)|$ is greatest.

Experiment Number	Experiment ID	surface wind orientation	shelf location	front zonal velocity (m s ⁻¹)
1	DF-F1	down-front	flat bottom	0.1895
2	DF-S	down-front	south	0.4047
3	DF-N	down-front	north	0.4086
4	UF-S	up-front	south	-0.2589
5	UF-N	up-front	north	-0.3694

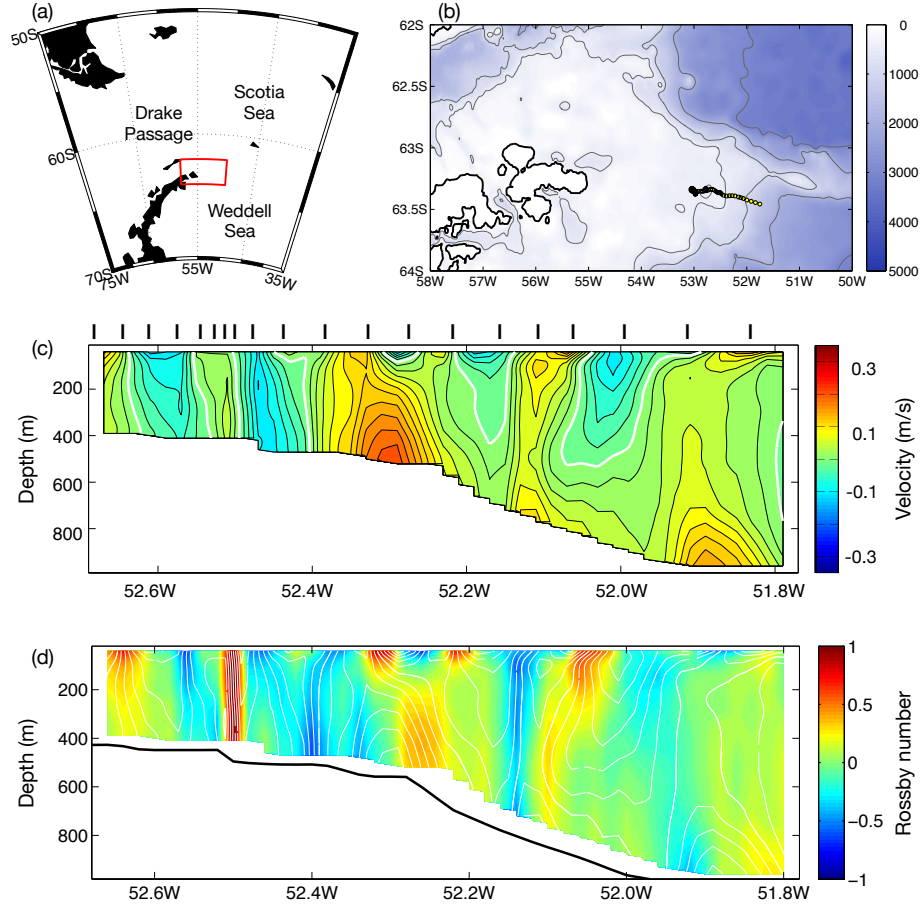


Figure 1: (a) Overview map of the Weddell Sea sector of the Southern Ocean. An enhanced view of the red box is shown in panel (b) where the bathymetry is given in color. The yellow dots in panel (b) correspond to a single hydrographic transect collected by an ocean glider in January 2012. Vertical, cross-slope section of (c) cross-track v (along-slope) velocity and (d) Rossby number approximated by v_x/f , where x is the off-shore direction. Tick marks at the top of panel (c) indicate the surfacing positions of each glider dive. See Thompson et al. (2014) for further details.

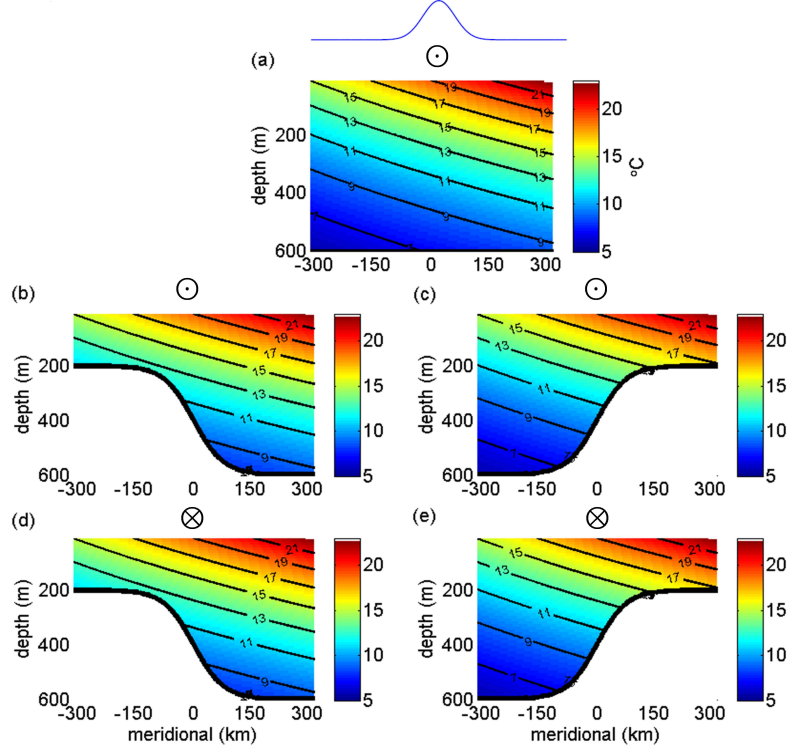


Figure 2: Schematic overview of the model configuration for the five simulations described in Table 1. Panels (a)-(e) correspond to experiments (1)-(5). Colors and contours show the zonally-uniform initial temperature profile. The temperature is relaxed to these initial values at the northern and southern boundaries. The thick black curve marks the bathymetry, while the circle over each panel marks the wind orientation: down-front (dots) or up-front (crosses). Blue curve on the top of panel (a) shows the surface wind stress profile, with a peak value $\tau_0 = 0.05 \text{ N m}^{-2}$.

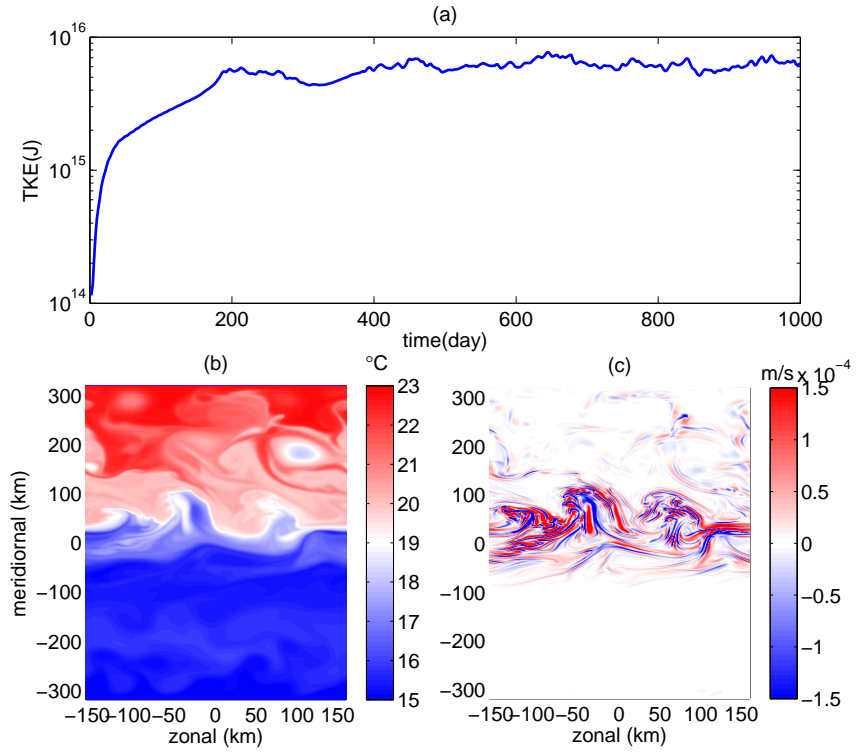


Figure 3: (a) Growth of total kinetic energy in Experiment DF-S. (b) Snapshots at day 900 for Experiment DF-S (Table 1) surface potential temperature ($^{\circ}\text{C}$) at 10 m depth. (c) Same as b, for vertical velocity w (10^{-4} m s $^{-1}$) at 30 m depth.

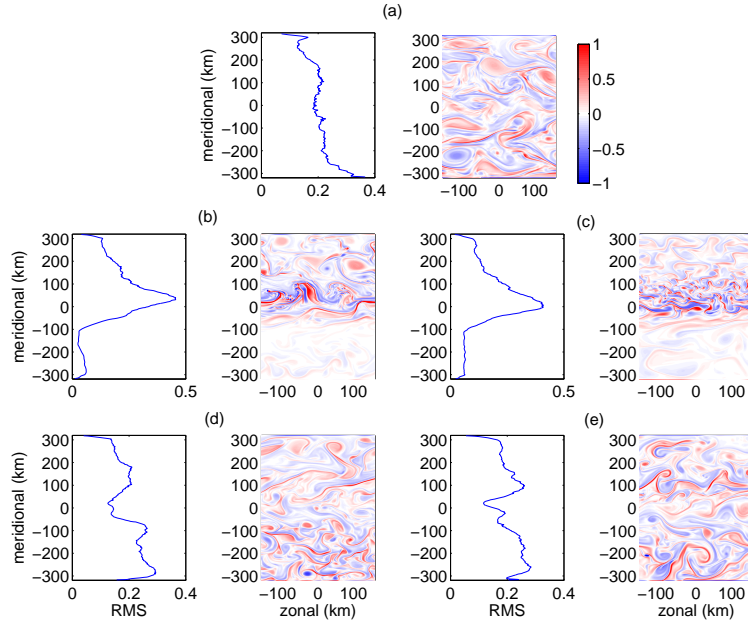


Figure 4: Near-surface Rossby number, $Ro = \zeta/f$, at 10m depth for the five experiments described in Table 1: (a) DF-F1, (b) DF-S, (c) DF-N, (d) UF-S, (e) UF-N. The left-hand plot in each plan shows the zonally-averaged root mean square (RMS) Ro averaged over a period of 200 days. The right-hand plot is a snapshot of surface Ro at day 900.

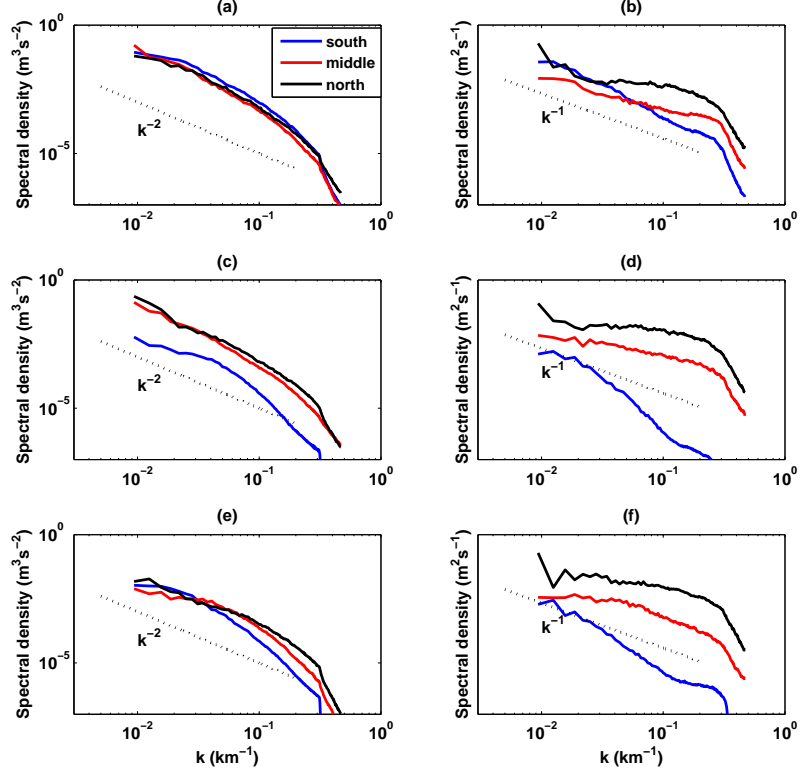


Figure 5: Spectra of surface horizontal kinetic energy (10 m depth, left panels) and vertical velocity (30 m depth, right panels) averaged from day 800 to 1000. (a) Kinetic energy spectra and (b) vertical velocity spectra in Experiment DF-FI. (c) Kinetic energy spectra and (d) vertical velocity spectra in Experiment DF-S. (e) Kinetic energy spectra and (f) vertical velocity spectra in Experiment DF-N. Dotted lines represent k^{-1} and k^{-2} spectral slope, provided for reference. Blue lines represent the southern flank of the domain from $-300 \text{ km} < y < -100 \text{ km}$. Red lines represent the middle of the domain (frontal region) from $-100 \text{ km} < y < 100 \text{ km}$. Black lines represent the northern flank of the domain from $100 \text{ km} < y < 300 \text{ km}$. Spectra in Experiments UF-S and UF-N are similar to those in the control Experiment DF-FI, and are not shown in this figure.

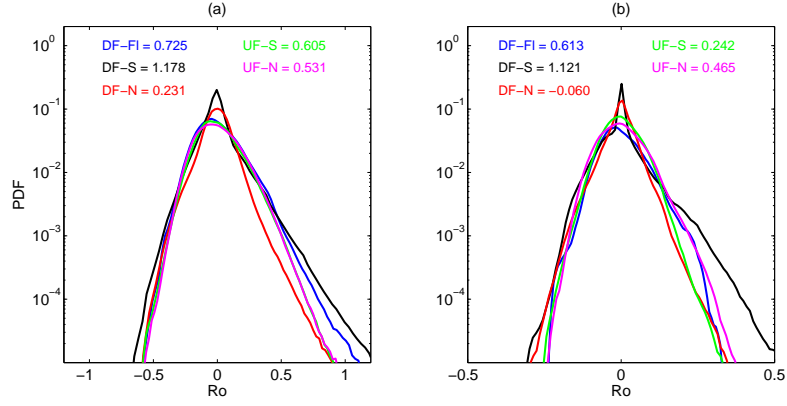


Figure 6: Probability density function (PDF) for (a) surface Rossby number, and (b) Rossby number at 180m depth averaged from day 800 to 1000 for Experiment (1) - (5). Values of PDF skewness are labeled using the same color for each Experiment.

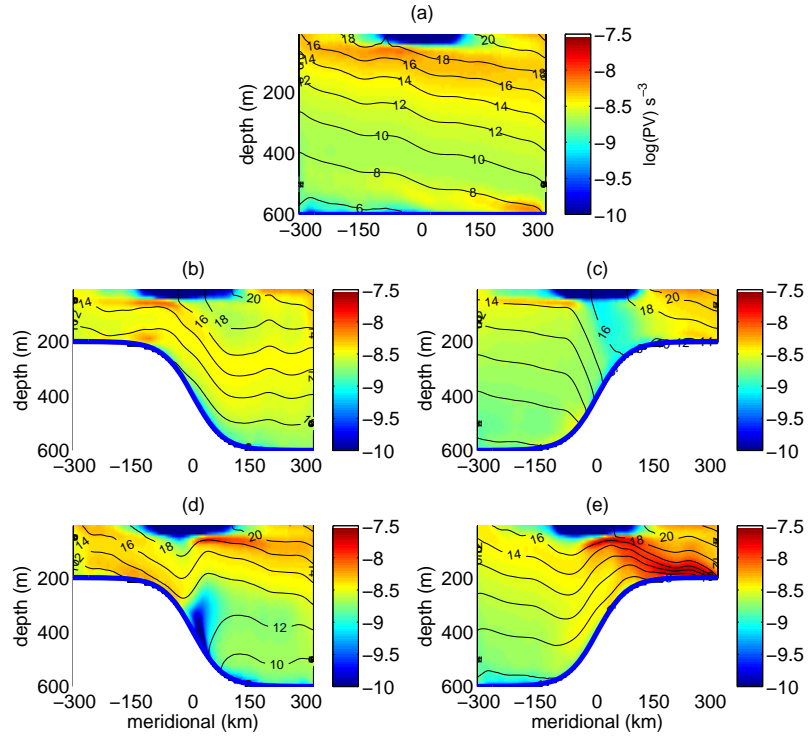


Figure 7: PV cross section in the middle of the domain ($x = 0$) averaged from day 800 to 1000 for five experiments. Values are displayed in \log_{10} scale. Black contours show the mean potential temperature, also indicate isopycnal surfaces.

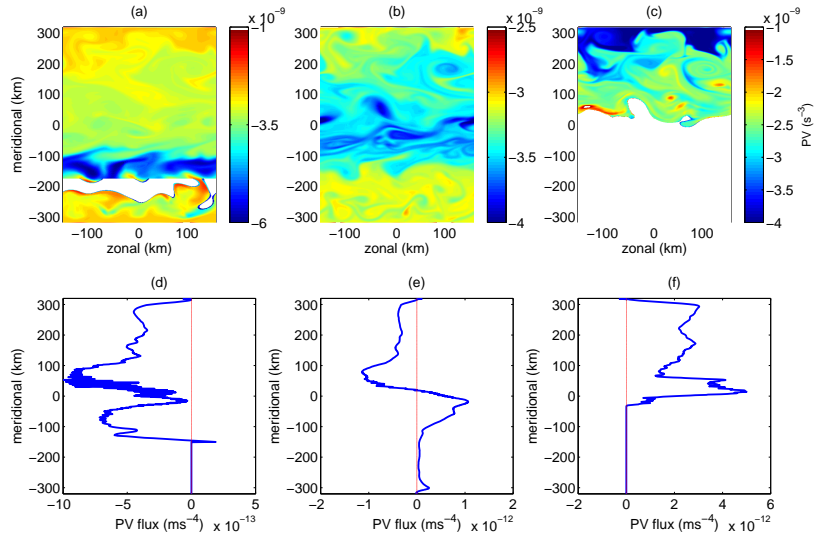


Figure 8: Upper panels are PV snapshots on the 12°C (a), 14°C (b), and 18°C (c) isopycnal surfaces at day 900 for Experiment DF-S. White areas indicate the isopycnal surface intersecting with the topographic slope or the surface. Lower panels are the corresponding time and zonal averaged PV fluxes. PV fluxes are calculated using snapshots between day 800 and 1000.

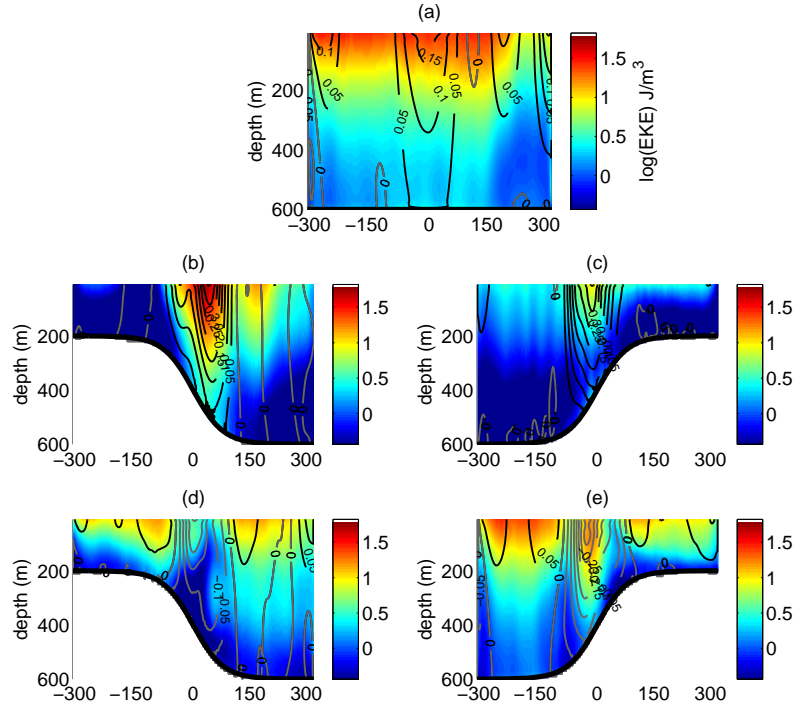


Figure 9: Zonal and time averaged EKE ($\rho(\mathbf{u}'^2 + \mathbf{v}'^2)/2$) from day 800 to 1000 for five experiments. Values are displayed in \log_{10} scale. Contour lines show zonal and time averaged zonal velocity (u). Black line represents positive values. Gray line represents negative values.

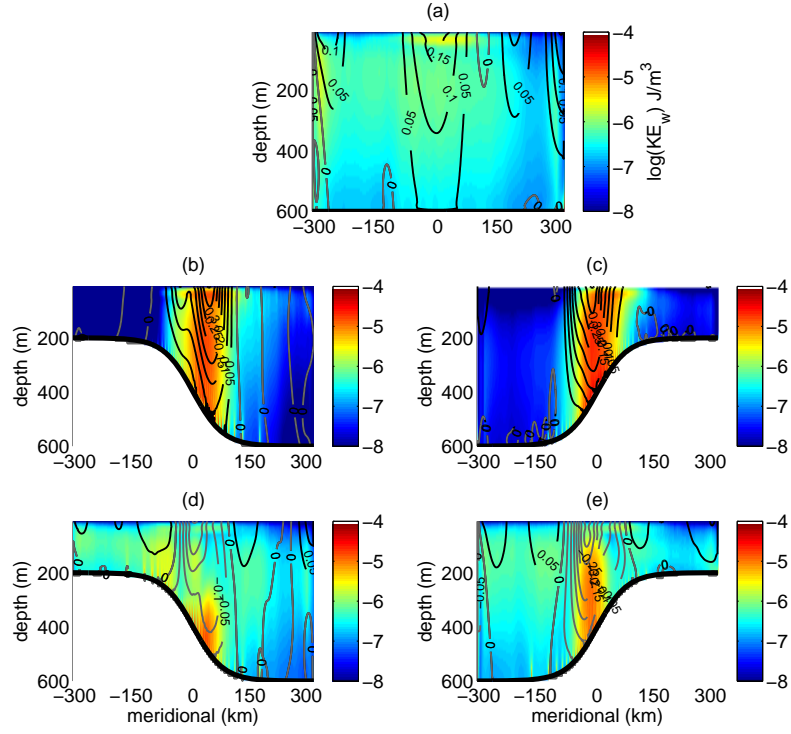


Figure 10: Zonal and time averaged vertical kinetic energy ($\rho \mathbf{w}^2/2$) from day 800 to 1000 for five experiments. Values are displayed in \log_{10} scale. Contour lines show zonal and time averaged zonal velocity (\mathbf{u}). Black line represents positive values. Gray line represents negative values.

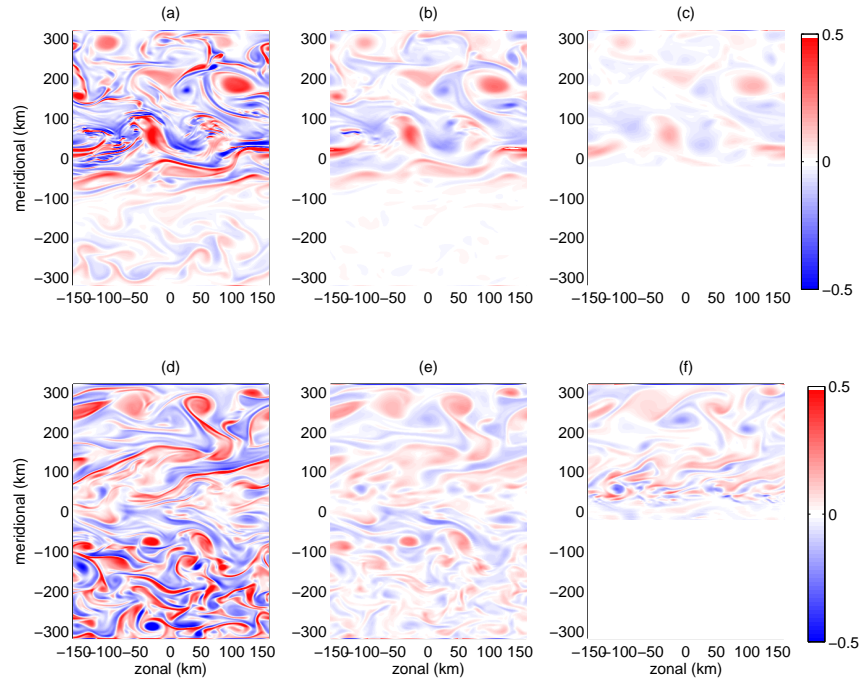


Figure 11: Vertical structure of Ro at day 900 for Experiment DF-S (a-c) and Experiment UF-S (d-f). Cross sections at 10m, 150m, and 300m depth are shown. White areas in (c) and (f) are associated with topographic slope interception.